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Evaluation of the Flux Chamber Method for Measuring Volatile Organic Emissions from Surface Impoundments

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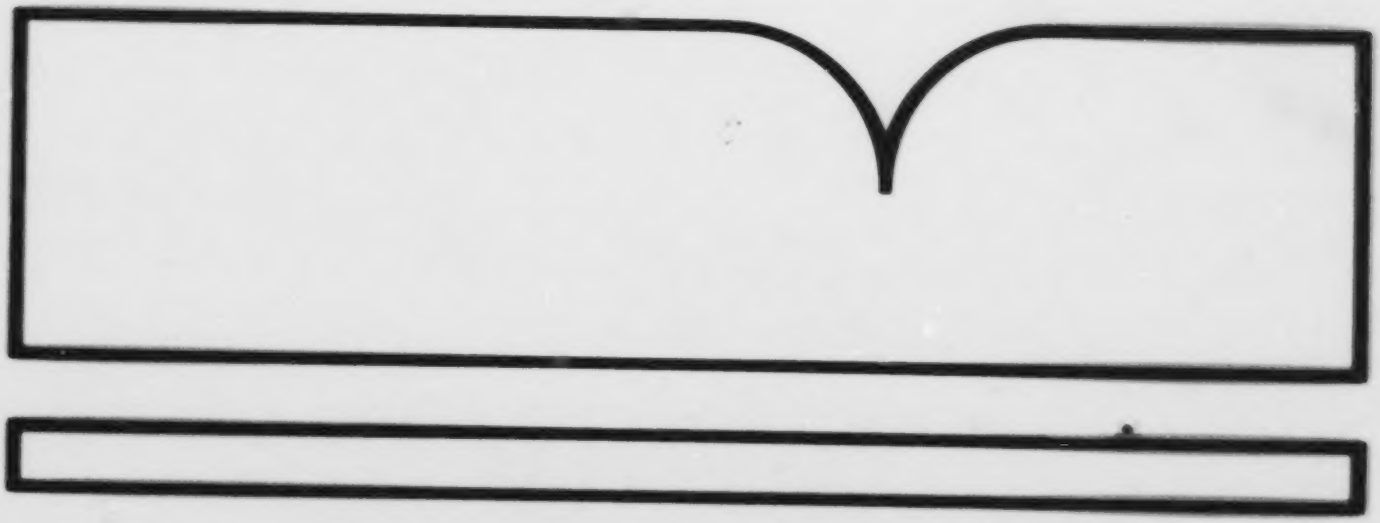

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EVALUATION OF THE FLUX CHAMBER METHOD FOR MEASURING VOLATILE ORGANIC EMISSIONS FROM SURFACE IMPOUNDMENTS

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16. ABSTRACT

This research deals with the validation of the flux chamber method for measuring volatile organic emissions from liquid surfaces in treatment, storage and disposal facilities (TSDF).

A simulated surface impoundment was constructed so that method precision and accuracy could be determined under controlled conditions. Operational parameters studied included sweep flow rate, sampling time, sweep flow position and chamber depth in the liquid. Environmental factors included wind velocity, solar intensity, emission rate, and chemical composition. Field testing was performed at two TSDFs, a wastewater treatment facility at a chemical plant, and a waste stabilization facility.

The results showed that good precision can be obtained under a variety of conditions, but that the method suffers from a negative bias that varies with the compound under analysis.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substance, and the Office of Solid Waste.

The exchange of organic chemicals across the air-water interface is a significant process affecting the transport and distribution of organic compounds in the environment. Emissions from liquid surfaces in treatment, storage and disposal facilities may be important sources of atmospheric contamination. The development and validation of measurement methods are key components in the assessment of such contamination, and for this reason, the present study has been conducted to validate a method employing an emission isolation chamber, or flux chamber to measure emissions from liquid surfaces. It was conducted at the request of the Office of Solid Waste.

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ABSTRACT

The overall objective of this research program was to estimate the precision and accuracy of the flux chamber method for measuring volatile organic emissions from open liquid bodies of waste during the treatment, storage, and disposal of hazardous waste.

A simulated surface impoundment was constructed so that the accuracy and variability of the method could be measured under controlled environmental conditions. Flux chamber operational parameters of sweep flow rate, sampling time, sweep flow position, and flux chamber depth were studied to determine their affect on precision and accuracy. Environmental factors of wind velocity, solar intensity, emission rate, and chemical composition were investigated. Precision of the method in the field was evaluated at two hazardous waste treatment, storage, and disposal facilities. One was a wastewater treatment facility at a chemical plant, and the other was a waste stabilization facility.

This report was submitted in fulfillment of Contract No. 68-02-4550 by Research Triangle Institute, under sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 15, 1986, to September 1, 1988.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Abbreviations and Symbols x
Acknowledgement xiii

1. Introduction 1
2. Conclusions 3
3. Recommendations 5
4. Background 6
5. Experimental Procedures 12
    General equipment 12
    Sample collection and analysis 16
    Laboratory experiments 22
    Field experiments 27
6. Results and Discussion 33
    Laboratory results 33
    Field experiments 51

References 63

FIGURES

Number		Page
1.	Schematic of flux chamber and support equipment	14
2.	Diagram of the surface impoundment simulator	15
3.	Schematic of Site One wastewater treatment facility	29
4.	Schematic of Site Two waste stabilization and treatment facility	31
5.	Measured emission rate versus sampling time	39

TABLES

Number		Page
1.	GC Conditions for Gas Analysis	20
2.	Parametric Study Experimental Conditions	24
3.	Precision and Accuracy Study Experimental Matrix	25
4.	Propane Tracer Study in the Flux Chamber	34
5.	Flux Chamber Outlet Position Study	34
6.	Propane Tracer Results for the SIS	35
7.	Results of Sweep Flow Rate Study	38
8.	Sweep Gas Inlet Height Results	41
9.	Results of Flux Chamber Depth Study	41
10.	Results of Flux Chamber Precision and Accuracy Study for 1,1,1-Trichloroethane	42
11.	Precision and Accuracy Estimate for 1,1,1-Trichloroethane	43
12.	Results of the Three-Component Precision and Accuracy Study	44
13.	Precision and Accuracy Estimates for Three-Component Emission Measurement	45

TABLES (Continued)

14. Results of Equilibrium Concentration Determination 46

15. Emission Rate Calculation Using Equilibrium Equation 48

16. Results of Wind Velocity and Solar Intensity Study 49

17. SIS Emission Rate Measured with Flux Chambers Present 50

18. Emission Results from Site One Field Evaluation 54

19. Results of Variation Analysis for Surface Impoundment Emission Measurements at Site One 55

20. Results of Variation Analysis for Open Overflow Channel Emission Measurements at Site One 55

21. Results of Daily QC Sample Analysis 56

22. Emission Rates Measured at the Primary Runoff Tank at Site Two 58

23. Emission Rates Measured at the Nonhazardous Storage Tank at Site Two 59

TABLES (Continued)

24. Results of Variation Analysis for the Primary Runoff Tank Emission Measurements at Site Two 60

25. Results of Variation Analysis for the Nonhazardous Storage Tank Emission Measurements at Site Two 61

26. Results of Sample Stability for Site Two 62

LIST OF ABBREVIATION AND SYMBOLS

ABBREVIATIONS

ACS	-- Americal Chemical Society
CL	-- confidence limit
CV	-- coefficient of variation
ECD	-- electron capture detector
EMSL	-- Atmospheric research and exposure assessment laboratory
FEP	-- fluorinated ethylene propylene
FID	-- flame ionization detector
GC/MS	-- gas chromatography/mass spectrometry
MEK	-- methyl ethyl ketone
NBS	-- National Bureau of Standards
OSW	-- Office of Solid Waste
PTFE	-- polytetrafluoroethylene
QC	-- quality control
RCRA	-- Resource Conservation and Recovery Act
RRF_T	-- relative response factors to toluene
RSD	-- relative standard deviation
RTI	-- Research Triangle Institute
SAS	-- Statistical Analysis System
SD	-- standard deviation
SIS	-- surface impoundment simulator
TCE	-- trichloroethane
TSDF	-- treatment, storage, and disposal facility
U.S. EPA	-- United States Environmental Protection Agency
UV	-- ultraviolet
VOC	-- volatile organic compound

SYMBOLS

A	surface area enclosed
C	gas-phase concentrations of the sample
C_g	concentration in the bulk gas
C_i	concentration of the emitted species
C_l	concentration in the bulk liquid
C_o	equilibrium gas-phase concentration
E	emission or flux rate
E_{fc}	flux chamber emission rate
E_i	emission rate of the emitted species
E_{sis}	average of the SIS emission rate calculated before and after the flux chamber measurement
f	sweep gas flow rate
$F_{propane}$	flow rate of propane
F_{sis}	SIS flow rate
H	Henry's law constant
k_g	gas-phase mass transfer coefficient
k_l	liquid-phase mass transfer coefficient
k_r	rate of recondensation
K	Von-Karmon constant
k_f	vaporization rate constant
K_L	total mass transfer coefficient
n	number of replicate measurements made
r_l	liquid film resistance
r_g	gas film resistance
R_L	total film resistance
Sc	Schmidt number
U	wind velocity at height Z

SYMBOLS

U^*	friction velocity
X	molefraction in the liquid
X_1	emission rate calculated using the first chamber
X_2	emission rate calculated using the second chamber
Z_o	effective roughness height

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SECTION 1

INTRODUCTION

During the treatment, storage, and disposal of hazardous waste, volatile organic compounds (VOCs) are released into the environment via the atmosphere. Under the 1984 Resource Conservation and Recovery Act (RCRA) Ammendments, the U.S. Environmental Protection Agency (U.S. EPA) is required to promulgate regulations for controlling these air emissions at hazardous waste treatment, storage, and disposal facilities (TSDFs). To support the regulatory process, analytical methods are required to measure or predict the emissions of VOCs from TSDFs, and the accuracy and precision of these methods should be well-characterized.

The U.S. EPA's Office of Solid Waste (OSW) has been involved in the activities to regulate the emission of organic pollutants into the environment from the handling, storage, and treatment of hazardous waste. One such activity involves a program to deal with emissions from impoundments and holding ponds at hazardous waste TSDFs. While participating in this program, the U.S. EPA's Atmospheric Research and Exposure Assessment Laboratory at Research Triangle Park, North Carolina, and the Research Triangle Institute (RTI), have undertaken to validate an isolation chamber device for measuring rates of emission from liquid surfaces.

The flux chamber method is an isolation chamber method that has been used to measure air emissions from surface impoundments, land farms, landfills, and contaminated soils. Emission measurements made with the

flux chamber are providing a data base for regulatory decision making, validating predictive air emission models, and assessing risk at Superfund cleanup sites. This report defines the quality of the data that can be obtained by using the flux chamber method to measure emissions from non-aerated surface impoundments and open tanks.

A combination of controlled laboratory experiments and field evaluations was performed to estimate the method's accuracy and precision. The influence of method parameters and environmental conditions was investigated to determine their effect on accuracy and precision. Single-compound and multicompound emissions were investigated in the laboratory with a simulated surface impoundment. Field evaluations were performed at two different sites on a range of liquid waste mixtures.

SECTION 2

CONCLUSIONS

The results of the laboratory and field evaluation of the flux chamber method indicate that liquid surface emission measurements can be made with very good precision, and that operational and environmental parameters have only a minor effect on the precision and accuracy. A compound-dependent negative bias ranging from 40 to 80 percent was evident during the laboratory studies. The source of this bias was investigated, but no definitive cause was determined.

The laboratory evaluation revealed that the flux chamber precision for a single compound was less than 3 percent relative standard deviation (RSD) under the ideal conditions of optimal sweep flow rate, steady solar conditions, and moderate to high emission rates. For the three-component study, precision was between 6 and 13 percent RSD. Precision was found to be only slightly influenced by sweep flow rates higher than 2 L/min, emission rate, and solar radiation. Sweep flow rates of less than 2 L/min should not be used for chambers of this design because of increased variability and poor accuracy.

Precisions estimated for the field evaluations were higher than those found in the laboratory study. The coefficients of variation (CVs) ranged from 3.5 to 19 percent for stable compounds when questionable flux chamber values were omitted. Variances as great as 30 percent were found when all flux chamber measurements were included. The added 10 percent variation caused by technical problems with the chamber illustrates the difficulty of performing flux chamber measurements in the field, especially when four measurements are being made simultaneously. Sample collection and storage accounted for 50 to 100 percent of the total variability, and instrumental analysis contributed less than 5 percent of the total. Variability between flux chambers accounted for the remaining percentage of the total

variability. When the variability due to sample collection and storage (which was required only for the field studies) is removed, the precision for the field study matched that in the laboratory study.

The negative bias during the laboratory studies is believed to be due to changes in the liquid turbulence caused by the flux chamber. Little change in the bias was detected over the range of wind velocities and solar intensities studied during this evaluation. Visible changes were noted in the liquid turbulence when the flux chambers were placed on the liquid surfaces. This change in turbulence and the magnitude of the change may be due to the large size of the flux chamber in relation to the experimental surface impoundment and the enclosure above it. The bias found for this study may not be valid for real conditions where the impact of the flux chamber would be considerably smaller because of the larger relative size of both the liquid surface and the air parcel surrounding it.

SECTION 3

RECOMMENDATIONS

The flux chamber method was found to be a reliable method for measuring volatile organic emissions from surface impoundments. Relative values for emission rates could be precisely determined and compared to other sources using the flux chamber. However, until the negative bias problem is resolved, the accuracy of the method is still questionable. Quantitative studies are needed to compare the effects of the flux chamber on surface turbulence in the field to those in the simulated surface impoundment to determine if the negative bias found in the laboratory is also present in the field.

Further method development may also be needed to improve the measurement variability found. New measurement methods are required to measure the emission rate of reactive volatile organics such as nitrobenzene and aniline using the flux chamber method.

Similar evaluations are needed to investigate the use of the flux chamber for measuring the emission rate of volatile organics from other hazardous waste treatment, storage, and disposal technologies such as land farms, landfills, and aerated surface impoundments. Other potential uses of the flux chamber should be investigated. Flux chambers could be used to evaluate potential emission reduction measures such as oil layers, protective barriers, and waste stabilization. Locating, mapping, and assessing the volatile emissions from leaking underground storage tanks by using flux chambers should be investigated. The flux chamber method may also be useful to measure the flux of toxic compounds in the indoor environment.

SECTION 4

BACKGROUND

Large quantities of liquid waste are being stored, treated, and disposed in surface impoundments, lagoons, open tanks, and other open bodies of water. The environmental and health risks due to the release of organic compounds into the atmosphere from liquid waste storage are currently being assessed, and regulatory options are being planned. One major problem with assessing these risks is the evaluation of exposure and levels of emission from liquid waste storage. In most cases, theoretical models have been used to predict the rate of emissions from open bodies of liquid waste. Many models have been proposed and used, and most are based on a similar theoretical approach; however, they all differ in the treatment and determination of the model parameters. Descriptions of some of these models have been published (1-6), and a protocol for using a prediction model for surface impoundments has been prepared for the U.S. EPA (7).

Efforts have been made to empirically measure the emission rate from liquid waste surfaces by using direct and indirect methods. Direct methods of measuring emissions include the isolation flux chamber method. Indirect methods for measuring emissions include the concentration-profile technique (1), mass balance approach, upwind-downwind sampling (8), and transect or plume profile technique. A review and evaluation of these techniques is available (9). The advantage of the direct method is that the critical parameters can be controlled and optimized so that an accurate analysis can be obtained. Indirect methods rely heavily on favorable meteorological conditions and detecting small concentration changes of analytes at very low levels. Errors due to unstable meteorological conditions and analytical uncertainties have resulted in a poor success rate for the indirect methods. The disadvantages of the direct method are the errors

that may be introduced by the disruption of the natural emission process caused by the enclosure.

Enclosure methods have been used to measure a wide variety of emissions from many different sources (10 - 15). The enclosure technique, moreover, has been adapted to measure the emission of organic pollutants from hazardous waste TSDFs (16, 17). The concept of the isolation flux chamber is relatively simple. A representative area of the source surface is enclosed by the chamber. Then a controlled flow of clean sweep gas is added to the chamber, allowed to mix, and then released through the chamber's exits. The concentrations of the emitted species are measured in the exit gas. The emission rates of the emitted species are calculated by using the following equation:

$$E_i = C_i \, f/A \qquad (1)$$

where f = sweep gas flow rate, L/min
A = surface area enclosed, m^2
C_i = concentration of the emitted species, mg/L
E_i = emission rate of the emitted species, $mg/min/m^2$

For the method to be accurate, two important assumptions must be valid:

1. The exit gas must have been well-mixed, and the emissions have reached a steady state when C_i is measured.

2. The chamber must not disturb the surface in a way that might increase or decrease the emission rate.

The first assumption can be evaluated with laboratory experiments, but the second assumption is much harder to evaluate. To understand what influences the volatile emission from a liquid surface, a brief discussion of the emission process is necessary.

The classical theory for describing the volatile emission from a liquid surface is the two-film or two-resistance theory (5). The theory describes the mass transfer occurring between two thin films of water and air at the water-air interface. These films, in theory, are in equilibrium with each other, and mass transfer is controlled by molecular diffusion to and from the interface. According to Fick's law of diffusion, diffusion is controlled by a diffusion coefficient and the differential in concentration; this is generally expressed in the following simplified equation:

$$E = K_L (C_g/H - C_l) \quad (2)$$

where E = emission or flux
K_L = total mass transfer coefficient
C_g = concentration in the bulk gas
C_l = concentration in the bulk liquid
H = Henry's law constant

Under most waste conditions on open liquid surfaces, C_l is much greater than C_g, and Equation (2) simplifies to $E = K_L C_l$; thus, one needs only to calculate K_L and measure C_l to estimate the flux. However, in the case of an enclosure method, C_g may not be much greater than C_l if the sweep gas flow rate is not high enough, and C_g may also be a significant flux controlling factor. Under ideal flux chamber conditions, K_L is the important factor.

The mass transfer process can also be viewed as a mass transfer resistance (R_L) by taking the reciprocal of K_L ($R_L = 1/K_L$). The total resistance is actually a sum of the resistance in the two thin films:

$$R_L = r_l + r_g \quad (3)$$

$$1/K_L = 1/k_l + 1/Hk_g \quad (4)$$

where r_l = liquid film resistance
r_g = gas film resistance
k_l = liquid mass transfer coefficient
k_g = gas mass transfer coefficient

Because of the large differences in k_l and k_g, in most cases R_L is completely dependent on either r_g or r_l. For volatile organic compounds where H is greater than 1×10^{-3} atm m^3 mol^{-1}, r_l is the controlling factor (18). Only for compounds that have either high liquid solubilities, low vapor pressure, or both does r_g become a controlling factor. So to understand how the flux chamber might affect the emission rate, the factors controlling r_l must be examined.

The liquid film resistance (r_l) or the liquid mass transfer coefficient (k_l) has been measured in the laboratory, and the effects of environmental factors have been studied (3, 6, 9, 19). The factors that were found to affect k_l are natural surface currents and convective motion. Surface winds are the most important factors influencing this turbulence.

A vertical mean logarithmic velocity profile is used to relate the wind velocity with turbulence factors:

$$U = (U^*/K) \ln Z/Z_o \quad (5)$$

where U = wind velocity at height Z
U^* = friction velocity
K = Von-Karmon constant
Z_o = effective roughness height

Z_o is related to the height of the chop or wave on the surface, and U^* is related to the drift velocity of the liquid surface. Experiments show that, at low wind speeds (U less than 3 m/s at Z = 10 m), k_l is little affected by wind speed, and internal mixing controls diffusion. At U between 3 to 6 m/s, the most common condition, a correlation between U^* and k_l was found (18). At higher wind speeds, large increases in k_l are found due to the breaking of waves.

Surface temperature affects diffusivity and viscosity, which in turn influence the liquid mass transfer. The Schmidt number (Sc) is used to account for solute diffusivity, liquid viscosity, and molecular size, all of which are dependent on temperature. As the temperature increases, Sc decreases, diffusivity rises, and viscosity falls. The mass transfer (k_l) has been shown by the following relationship to increase with temperature as Sc decreases :

$$k_l \propto Sc^{-0.5} \quad (6)$$

By combining the wind variable and the diffusion variable, an empirical formula (or formulas) for k_l has been suggested:

$$k_l = 10^{-6} + 144 \times 10^{-4} U^{*2.2} Sc^{-0.5} \quad (U^* < 0.3 \text{ m/s}) \quad (7)$$

$$k_l = 10^{-6} + 34.1 \times 10^{-4} U^* Sc^{-0.5} \quad (U^* > 0.3 \text{ m/s}) \quad (8)$$

Placing a flux chamber on a liquid surface will affect the U^* and the temperature to some extent. Because the turbulent motion of the surface is a result of large-scale processes, the flux chamber effect may be minimal. The air temperature increase predicted by the greenhouse effect inside the

chamber may raise the surface temperature and cause an increase in emissions. However, by optimizing sweep flow and keeping the enclosure period to a minimum, the surface heating due to the increased air temperature can be kept to a minimum.

In addition to the effects the flux chamber may have on the mass transfer coefficient, the liquid-gas phase equilibrium may be affected if gas-phase concentrations in the chamber are too high. The flux of a compound in the chamber can be expressed by the equation:

$$dn/dt = k_f XA - k_r C_g A - C_g f \quad (9)$$

where k_f = vaporization rate constant
X = mole fraction in the liquid
A = surface area
k_r = rate of recondensation
C_g = concentration in the bulk gas
f = sweep flow rate

At a steady state, $dn/dt = 0$ and the equation can be rewritten:

$$k_f XA = k_r C_g A + C_g f \quad (10)$$

When sweep flow is zero, equilibrium is reached, and the equilibrium gas-phase concentration (C_o) can be calculated:

$$C_o = k_f XA/k_r A = HX \quad (11)$$

where H is the Henry's law constant, as previously defined in Equation (2). Assuming $k_f X$ is equal to the emission rate (E) and substituting C_o and E into Equation (10), the following is found:

$$1/C_g = 1/C_o + f/EA \quad (12)$$

and solving for E

$$E = f/A\ (1/C_g - 1/C_o)^{-1} \quad (13)$$

When C_g is much greater than C_o, then Equation (13) simplifies to the flux chamber emission rate of Equation (1). Before the assumption that C_g is much greater than C_o can be made, C_o must be known under experimental conditions. For ideal conditions, H can be found in tables and C_o can be calculated, but experimental values may differ widely. If the assumption $C_g \gg C_o$ cannot be made, C_o can be used to calculate the emission rate by using Equation (13), or alternatively, $1/C_g$ can be plotted versus f, and E

can be calculated from the slope (1/EA).

The laboratory experiments for this evaluation have been designed to address these concerns over the flux chamber's accuracy. A true emission rate has been measured and compared with the rate measured by the flux chamber. Moreover, parametric studies have been conducted to assess the effect of critical flux chamber and environmental parameters on the method's accuracy.

SECTION 5

EXPERIMENTAL PROCEDURES

GENERAL EQUIPMENT

To perform the method evaluation, four flux chambers were constructed including the ancillary equipment required during laboratory and field testing of the method. A surface impoundment simulator (SIS) was also constructed to provide a controlled environment similar to field conditions where actual emission rates could be measured.

Flux Chamber Design

The flux chamber design used in this study is that described by Kienbusch and Ranum (20) with several minor modifications. The base of the chamber was a cylinder 0.41 m in diameter, 0.18 m long, and constructed of stainless steel. The top of the cylinder was covered with a clear 3.2-mm-thick acrylic dome with a maximum height of 0.10 m. The dome was attached to the base with an aluminum flange and polytetrafluoroethylene (PTFE) gasket. Four equally spaced holes in the dome provided an inlet for sweep gas, an outlet for sample gas, wiring for temperature probes, and a vent for excess sweep gas. No mechanical impeller was used for mixing because several previous studies have shown that the impeller had no significant influence (15) or added a positive bias (20) to the emission rate. Complete mixing was demonstrated without an impeller in a similar flux chamber design (16). The sweep gas inlet tube skirted the base below the dome with gas exiting from four equally spaced holes pointing toward the center of the chamber. The height of the tube could be adjusted to study its effect on the measured emission rate. The sample exit line extended from 10 cm above the base opening to 2.5 cm from the top of the dome, and it was positioned so that it was equally distant from two sweep inlet holes and halfway between the center of the chamber and the chamber wall. The

exit line was perforated with two columns of holes that faced perpendicularly to the flow of the sweep gas. For the laboratory study, the flux chamber was supported on the liquid surface by two handles on the outside of the chamber base. For the field studies, three 0.093-m^2 polyethylene foam floats were used to support the flux chamber. A removable aluminum collar was used to extend the floats 0.46 m from the chambers and was adjustable to set the depth of the chamber base in the liquid. Two thermocouples were placed inside the chamber supported by a piece of PTFE tubing so that one measured the bulk air temperature inside the chamber, and the other measured the temperature at the liquid surface inside the chamber. Figure 1 is a schematic of the flux chamber and the support equipment.

The flux chamber was supplied with a source of nitrogen or hydrocarbon-free air for the sweep gas. The sweep gas was regulated and the flow rate was controlled. A calibrated mass flow meter was used to monitor the sweep flow rate in the laboratory studies, and a calibrated bubble flow meter was used to check the sweep flow rate in the field. In the field, the sweep flow was supplied to the chambers with a 25-m length of 3.1-mm-o.d. fluorinated ethylene propylene (FEP) tubing. Shorter lengths of 6.2-mm PTFE tubing were used in the laboratory studies.

The gas taken for sample analysis was drawn from the chamber with a diaphragm vacuum pump. A tee was placed before the pump to allow samples to be removed for analysis by either a syringe or an evacuated canister. The sample flow rate was controlled with a metering valve at a rate of approximately 150 mL/min. A differential pressure gauge was used periodically to determine if any pressure buildup was occurring inside the chamber. A 25-m length of 3.1-mm-o.d. FEP tubing was used to transfer the sample to the pump in the field, and a shorter length of 6.2-mm-o.d. FEP tubing was used in the laboratory.

The flux chamber temperature was monitored with type J thermocouples connected with 25 m of thermocouple cable to a multichannel monitor. For the laboratory studies, the thermocouples were connected directly to the temperature monitor.

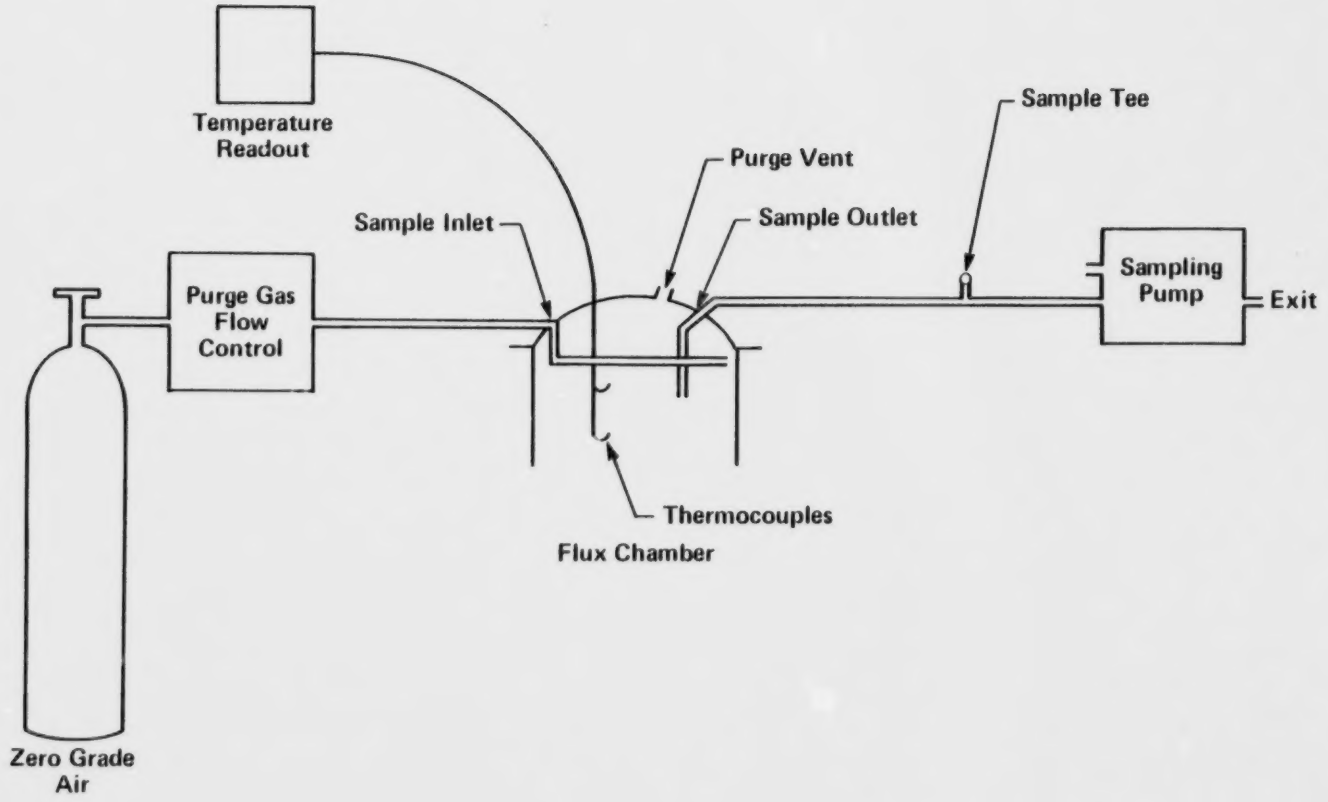

Figure 1. Schematic of flux chamber and support equipment.

Surface Impoundment Simulator

The SIS consisted of a 0.83-m^3 (220 gal) rectangular tank covered with an aluminum frame wrapped with clear FEP film. One end of the cover was open to the atmosphere through a series of honeycombed openings, and the other end was attached to a reducing duct connected to the inlet of a blower. Figure 2 is a diagram of the SIS. The tank surface was 1.2 m by 1.5 m (1.86 m^2), and it had a maximum depth of 0.61 m and a minimum depth of 0.30 m. The tank was constructed of galvanized steel and supported with six legs resting on concrete blocks.

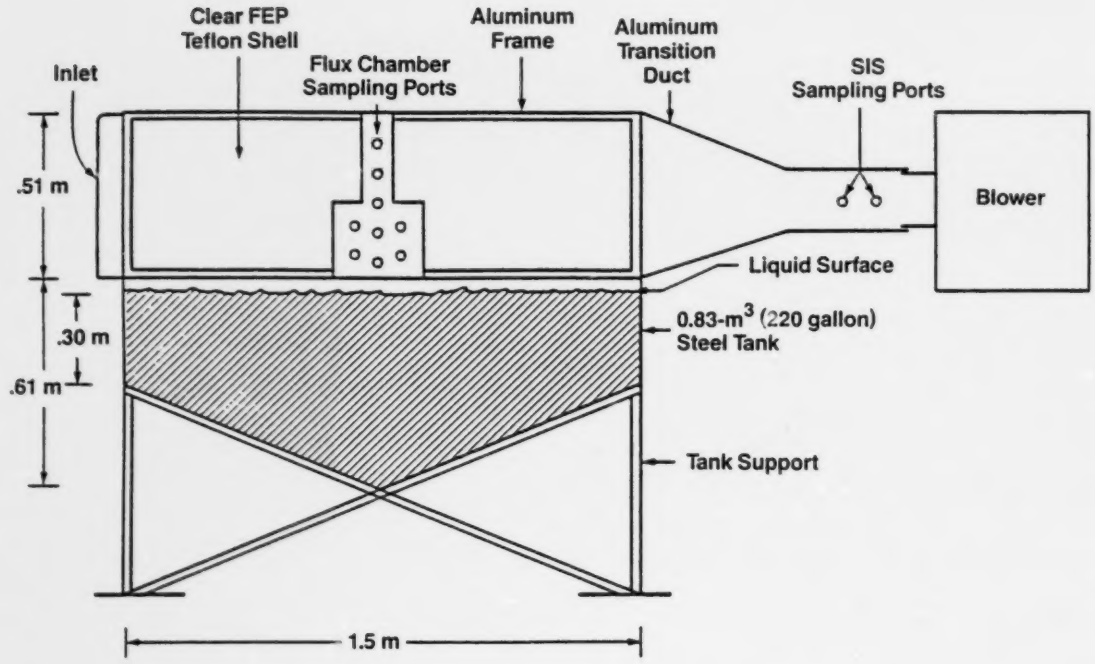

Figure 2. Diagram of the surface impoundment simulator.

The SIS cover was a rectangular box that was 0.51 m high, 1.3 m wide, and 1.6 m long. The two sides and top were covered with 0.13-mm-thick FEP film. One side of the cover was connected to the tank with a hinge to allow easy access to the tank surface. An aluminum panel on the side of the cover opposite the hinge had fittings to connect the flux chamber's sweep gas, sample gas, and thermocouples. Additional thermocouples were placed inside the cover to monitor the bulk air temperature in the SIS and the liquid surface temperature outside the flux chamber.

An aluminum duct was used to reduce one end of the cover into a 20-cm diameter pipe, where it was connected to a direct drive blower with a free-air pumping capacity of 28.3 m^3/min. Two 8-mm-o.d. stainless steel Pitot tubes were mounted in the pipe leading from the duct work to the blower to measure the air velocity. An air sampling port, consisting of a stainless steel tube extending 10 cm into the pipe, was placed just downstream from the Pitot tubes. A flow dampener was placed between the Pitot tube and the blower to control the air velocity in the SIS.

Organic compounds were added to the SIS in solutions that were denser than water so that amounts exceeding the solubility would remain at the bottom. An excess of 1,1,1-trichloroethane was always present, and a window was placed at the bottom of the tank to monitor the level of the organic layer. When toluene and methyl ethyl ketone (MEK) were added for the three-component study, a mixture in 1,1,1-trichloroethane was added through a tube submerged under the organic layer. This prevented an organic layer from forming on the surface and ensured a constant supply of organic material to the bulk solution. American Chemical Society (ACS) reagent- grade chemicals were used in the SIS. Normal tap water was used to fill the SIS tank to within 2.5 cm of the top.

SAMPLE COLLECTION AND ANALYSIS

Two sample collection methods were used during the flux chamber evaluation. A simple grab sample collected in a glass syringe was used during the initial parametric studies and the precision and accuracy study. Two samples were collected over a 10-min period, and the results were averaged. The syringe method was easy and provided good results if the analysis was performed within 30 min after collection. Evacuated, electropolished stainless steel canisters were used to collect 10-min integrated samples.

The integrated sampling provided a more accurate estimate of an average emission than did the grab samples if the emission rate was changing rapidly because of such factors as turbulence or solar fluctuations. Samples collected in the canister were found to be stable for up to two weeks, which was convenient for the field experiments where samples had to be brought back to the laboratory for analysis.

Glass Syringe Sampling

Two types of syringes were used to collect flux chamber and SIS samples during this evaluation. A 100-mL glass and PTFE gas-tight syringe were used initially, but problems were found with cleaning the syringe between analyses due to the PTFE parts. An all-glass 50-mL syringe with a ground glass plunger was also used. Although the syringe was not completely gas-tight, samples could be safely stored for up to 30 min. No carryover between samples was found after three rinses with clean nitrogen when the all-glass syringe was used. Syringe samples were collected from either the tee in the flux chamber sample gas line or the sample probe in the SIS exhaust duct. For both samples, stainless steel needles were used to collect the samples through silicone septa. Samples were hand-drawn with the plunger at a steady rate of approximately 100 mL/min.

Canister Sampling

For the later laboratory studies (wind velocity and solar intensity experiments) and all the field studies, samples were collected in evacuated 2-L, electropolished stainless steel canisters. The canisters were cleaned by repeated pressurization with nitrogen and evacuation to less than 1 mm H_g at 150 °C. Every fourth canister was blank checked by analyzing >100 mL of nitrogen stored in the canister for over an hour. Before using the canister, each one was leak checked by evacuating the canister and checking the pressure 24 h later. Final evacuation of the canisters was performed just before sample collection for laboratory studies and at the latest possible time before they were shipped from the laboratory for field studies.

Sample collection using the canister was controlled by a calibrated restrictor prepared from a piece of stainless steel capillary tubing (0.2 mm i.d.). Each restrictor was calibrated by using an evacuated canister

and measuring the pressure change as a function of time. Restrictions were chosen so that a constant flow rate of 100 mL/min was maintained for 10 min with a 2-L canister. The restrictor and canister were connected to the flux chamber sample gas tee or the SIS sample probe, and the valve on the canister was opened for a period of 10 min to collect the sample. For duplicate samples, two canisters were connected to the sample line, and both valves were opened for the same period. The flow exiting the flux chamber sample pump was monitored with a rotameter to ensure that the canister sample was not being drawn through the pump.

Before the canister samples were analyzed, the final pressure was recorded, and the canister was pressurized to approximately 200 kPa with nitrogen. The sample dilution factor was calculated by dividing the pressure collected (final pressure - initial pressure) by the absolute pressure to which the sample was pressurized.

Liquid Sampling

Liquid samples were collected by lowering a stoppered 8-mL sample vial into the liquid to the desired sampling depth and filling the vial by removing the stopper. The vial was resealed with an FEP-coated septum, leaving no headspace, and stored at 4 °C until analyzed. Because of the distances between the flux chamber and the point where surface samples could be collected during the field studies, no meaningful liquid surface samples could be collected. At Site One, PTFE bailers that were attached to two of the flux chambers and collected a liquid sample below the surface. The bailers proved to be unsatisfactory because they did not collect the surface liquid layer but instead collected large quantities of sediment from the bottom of the pond.

Gas Analysis

Gas samples collected from the flux chamber and the SIS were analyzed by gas chromatography (GC) with either a gas sampling valve or a preconcentration step. A six-port valve with a 2-mL stainless steel loop was used for most of the laboratory studies where sample concentrations were greater than 10 ppmV. The sample was purged through the loop from a syringe or pressurized canister before switching the valve and injecting the sample onto the column.

For samples where the concentrations were less than 10 ppmV, preconcentration was necessary. Both adsorbent and cryogenic trapping were used to preconcentrate samples during this study. For the earlier laboratory studies, syringe SIS samples were concentrated on a Tenax solid adsorbent trap. Between 50 and 100 mL of sample were injected at approximately 50 mL/min into a stream of nitrogen flowing at 60 mL/min onto the adsorbent trap. The lines were swept for 4 min to ensure that all the sample was on the trap. The trap was thermally desorbed at 185 °C directly onto a packed column with a carrier flow rate of 40 mL/min.

All the field samples were preconcentrated by using a trap packed with 60-80 mesh silanized glass beads and cooled to -186 °C with liquid argon. A calibrated vacuum ballast system was used to meter the volume of sample concentrated. Boiling water was used to rapidly desorb the sample onto a capillary column. Cryogenic concentration was used for field samples because the solid adsorption characteristics of unknown compounds encountered in the field samples may not have been favorable, and cryogenic concentration allowed capillary columns to be used to improve the resolution of the complex mixtures found in the field samples.

A Perkin-Elmer 3920B GC with a flame ionization detector (FID) and an electron capture detector (ECD) were used for all gas analyses. Table 1 lists the GC conditions used to analyze samples with both a packed column and a capillary column. The capillary column was used for the field studies and the wind velocity and solar radiation laboratory studies. The FID was used for peak quantification unless an interference was observed or the response was too small; then the ECD was used. An electronic integrator was used to record the peaks and calculate the area for all analyses.

Liquid Analysis

Liquid samples from the SIS were analyzed by direct aqueous injection with a 10:1 split into a 30-m, 0.53-mm-i.d. DB-1 Megabore fused-silica capillary column (J & W Scientific). A Tracor 560 GC with an FID was used for all liquid analyses. The temperature program used an initial value of 70 °C held for 2 min and then programmed to 180 °C at 16 °C/min. An electronic integrator was used to quantify the FID responses for all analyses. Liquid field samples could not be analyzed by direct injection because of the chemical nature of the matrix. Purge-and-trap analyses were

TABLE 1. GC CONDITIONS FOR GAS ANALYSIS

Parameter	Packed column	Capillary column
Column	3-m 1% SP1000 on Carbopack 80/100 mesh	30-m DB624 Megabore 1.5-mm film, 0.53-mm-i.d.
Carrier gas	N_2, 40 mL/min	He, 5 mL/min
Oven program		
Initial temperature	55 °C	10 °C
Initial hold	2 min	2 min
Program rate	32 °C/min	8 °C/min
Final temperature	210 °C	185 °C
Detector	FID	FID and ECD split 5:1

performed on the samples collected by using a Tekmar liquid sample concentration model LSC-2 and the standard EPA Method 601 protocol, with the exception of the use of an FID.

Standards

Gas analyses for the laboratory study were calibrated by comparing sample responses with external standard responses. Gas standards were prepared by flash evaporating a known amount of each compound. The vaporized components were purged with nitrogen into an evacuated canister of a known volume. Standards were prepared at three concentrations covering the range of concentrations expected to be found in the samples. All propane samples were calibrated using standards certified against an NBS (National Bureau of Standards) standard reference material.

For the field studies, a combination of commercially prepared standards and standards prepared by the above method were used. Two commercially prepared standards were used for samples collected at Site Two. Because of the continually changing composition of the emission sources at Site Two, an 18-component standard at concentrations of 5 ppbV was used to calibrate the analyses. The standard was certified by the manufacturer, and a comparison was made with NBS primary standards (21). For compounds identified in the sample but not in the standard, canister standards were prepared containing these compounds and toluene (which was

present in the 18-component standards). Values for the relative response factor to toluene (RRF_T) were then calculated from replicate analysis of the canister standard for the identified sample compounds. The RRF_T values were then used with the toluene response from the original calibration to quantify the identified sample compounds. For Site One, the major compounds were identified during a presite survey, and canister samples were prepared to calibrate the analysis.

In addition to the calibration standards, quality control (QC) standards were prepared for each field study. For Site One, a standard prepared in a canister containing the compounds identified during the presite visit was used as the QC standard. At Site Two, a certified, commercially prepared standard containing 5 compounds present in the 18-component standard was used as the QC standard.

Emission Measurement Procedure

A standard procedure was followed throughout the laboratory and field evaluations to measure the VOC emission rate inside the flux chamber and the total emission from the SIS. Different operating parameters of the basic method were changed during the laboratory evaluation as described in the section below.

Flux chamber emissions were measured by initially purging the chamber and lines with sweep gas at the specified flow rate, and with the sample purge pump running while the flux chamber was suspended above the liquid surface. The chamber base was then placed on the surface to the specified depth with sweep gas flowing, and a timer was started. The chamber base was checked to ensure that it was completely and evenly submerged. At the specified sampling time or times, a syringe or canister was used to collect a sample from the sample tee. While the sample was collected, temperature readings were recorded. After the sample was collected, the flux chamber was lifted from the surface and purged before another measurement was made.

SIS emission measurements were initiated by closing the tank cover and starting the blowers. The blower was run for 10 min to allow for the flow patterns to reach a steady state. The sample was then collected by either a syringe or canister from the sampling port in the blower duct. A

Pitot reading was taken from the center position of the blower duct, and SIS surface and bulk air temperature readings were recorded.

Emission rates for both the SIS and the flux chambers were calculated from the measured VOC concentrations in the sample collected by using:

$$E = f\ C/A \qquad (14)$$

where E = emission rate, $mg/min/m^2$
f = sweep flow or SIS flow rate, L/min
C = gas-phase concentrations of the sample, mg/L
A = surface area of the flux chamber or SIS, m^2

LABORATORY EXPERIMENTS

The first purpose of the laboratory experiments was to determine if the flux chamber and SIS were performing properly. A series of mixing studies and flow rate determinations was made using the SIS and the flux chambers. The second purpose for the laboratory studies was to determine what effect the flux chamber's operating parameters had on the measured emission rate. The third purpose was to estimate the method's precision and accuracy and to determine how several operating and environmental parameters affected the quality of the method's data. The final purpose of the laboratory studies was to find the cause of the consistent, negative bias found during the accuracy studies.

Flow Rate and Mixing Studies

Because knowing the true flow rate and obtaining a well-mixed sample in the SIS and flux chambers were so critical for evaluating the accuracy and precision and for obtaining data with good accuracy and precision, several methods were used to confirm the flow rates and mixing efficiency. Two independent methods were used to determine the flow rate of air through the SIS. One method physically measured an averaged air velocity that was translated into a flow rate, and the second method determined the flow rate indirectly by using a chemical tracer. The two standard Pitot tubes mounted in the blower duct were used to traverse perpendicularly the airstream and measure the air velocity from the center of the duct to 1.6

mm from the sides. From the traverse data, an average velocity was calculated. The ratio of the average velocity versus the air velocity measured in the center of the duct was calculated. This ratio or correction factor was then used to determine the flow rate from a single velocity measured in the center of the duct.

A chemical tracer method was used to provide a third measurement of SIS flow rate and to ensure that complete mixing of the air in the SIS occurred at the sample port. Pure propane was released continually into the SIS at a series of flow rates ranging from 200 to 500 mL/min. Samples were collected from the sample port and analyzed. Assuming complete mixing, the flow rate in the SIS was calculated from the measured dilution of the propane. Complete mixing of the SIS air was checked by varying the position of the sample port inside the blower duct. Samples were collected 1.9 cm from the bottom wall, 10 cm from the side wall, and 1.9 cm from the side wall.

Mixing studies for the flux chamber were performed by using a propane tracer. Pure propane was introduced into the chamber above the liquid surface at three different flow rates (2, 5, and 12 mL/min). Samples were collected and analyzed to compare the concentration measured with the theoretical concentration which was calculated from the propane flow rate and the flux chamber flow rate. Stratification of concentrations inside the chamber was checked by collecting a sample from three separate points at varying heights in the flux chamber and comparing the results to a second flux chamber sampling with the standard sample probe.

Flux Chamber Parametric Studies

The effect on the measured emission rate of a series of experimental parameters was investigated. The parameters studied were sweep flow rate, sampling time, height of sweep flow above the liquid surface, and flux chamber depth. Emission rates were measured by using two chambers, one in which the parameter was kept constant and one in which the parameter was varied. For all the parametric studies except the depth study, a single volatile compound (1,1,1-trichloroethane) was present in the SIS. Table 2 is a list of the parametric studies and the conditions used.

TABLE 2. PARAMETRIC STUDY EXPERIMENTAL CONDITIONS

Study	Parameter setting			
	Sweep flow (L/min)	Sample times (min)	Inlet height (cm)	Chamber depth (cm)
Control	5	20,30[a]	12	1.3
Sweep flow	1,2,3,5,7,9,10	20,30	12	1.3
Sample time	5	8,16,24,32,40,45,56,64,72	12	1.3
Inlet height	5	20,30	2,6.4,10	1.3
Chamber depth	5	20,30	12	1.3, 2.5, 5.1 8.9

[a]No control was run for the sample time study.

The sweep flow rate study was made with the 1, 2, 5, and 10 L/min points collected by using one chamber as the control and by using the other as the control chamber to measure the 3, 7, and 9 L/min points. A differential pressure measurement was made at each flow rate to determine if an increase in pressure occurred.

The time study was made to determine if the measured emission rates changed as a function of time that the chamber covered the liquid surface. Measurements were made in the full sun and on a completely overcast day. No control was possible for this study, so duplicate chamber measurements were collected at each sampling time.

Because the inlet height of the sweep gas might affect the surface wind velocity inside the flux chamber, the inlet height was varied and emission measurements were made. The chamber depth may have affected the liquid-phase diffusion and liquid surface drift velocity, so the insertion depth was varied and measurements were made. Changing the insertion depth also effectively changed both the sweep gas inlet height above the liquid surface and the volume of gas in the flux chamber.

Precision and Accuracy Study

A series of duplicate flux chamber measurements was made by using the same operating parameters to determine the accuracy and precision of the method. A series of duplicate measurements was made for single-component

TABLE 3. PRECISION AND ACCURACY STUDY EXPERIMENTAL MATRIX

Number of compounds	Sweep flow (L/min)	Time of day	Number of replicates
1	5	Day	12
1	2	Day	3
1	10	Day	3
1	5	Night	3
3	5	Day	9

measurements and three-component measurements, during daylight hours and at night, and at three different sweep flow rates. Table 3 lists the number of measurements made under the environmental conditions and the operational parameters listed. A sweep inlet height of 10 cm, a chamber depth of 1.3 cm, and an average of two samples at a sample time of 20 and 30 min were used for all the accuracy and precision measurements. Each duplicate flux chamber measurement was bracketed with before and after total SIS emission measurements to obtain a true emission rate for an estimate of method accuracy.

The method precision was calculated by estimating the standard deviations of duplicate measurements for replicate sets under similar environmental and operational conditions as described by Taylor (22). The following equation was used to calculate the standard deviation (SD):

$$SD = \sqrt{\sum_{i=1}^{i=n} \frac{(X_{1i}-X_{2i})^2}{2n}} \qquad (15)$$

where X_{1i} = emission rate calculated by using the first chamber
X_{2i} = emission rate calculated by using the second chamber
n = number of replicate measurements made

The accuracy of the method was determined by calculating the percent bias between the average of the duplicate flux chamber measurement and the average of the before and after SIS measurements by using the following equation:

$$\% \text{ Bias} = \frac{E_{fc} - E_{sis}}{E_{sis}} \times 100 \qquad (16)$$

where E_{fc} = average measured emission rate from duplicate flux chambers
E_{sis} = average emission rate from the SIS before the flux chamber measurement and after the flux chamber measurement

Separate accuracy and precision estimates were made for each set of conditions listed in Table 3.

Negative Bias Investigation Studies

After the results of the precision and accuracy studies were obtained, a consistent, negative bias was discovered for the flux chamber method. Several reasons for this bias were proposed, and experiments were performed to investigate these possible explanations. These included, first, that the gas-phase equilibrium concentrations were being approached inside the flux chamber, which was inhibiting the emissions from the liquid phase. The second explanation was that the gas velocity above the liquid surface was substantially different in the SIS than inside the flux chamber, thereby causing the difference in the measured emission rate. The third explanation was that the transfer of solar radiation through the FEP film of the SIS was greater than through the flux chamber's acrylic dome, thus resulting in increased evaporation and volatile emissions outside the flux chamber. The fourth explanation was that the presence of the flux chamber on the surface of the liquid was disrupting the movement of liquid that controlled the liquid diffusion of the organic compounds to the surface, which may be the rate-controlling step in the overall emission process.

Equilibrium Concentration Experiment--

To determine if the emission rate inside the flux chamber was being inhibited by the high concentrations accumulated inside the chamber, the chambers were placed on the liquid surface with no sweep flow, and small volumes of samples were periodically removed and analyzed until a constant concentration was reached. The SIS liquid concentration of the three compounds was also calculated near the surface. The liquid-gas-phase partition coefficient was calculated and compared with literature values for the three compounds. The emission rate was then remeasured with the flux chambers at a sweep flow rate betwen 0.5 and 9 L/min. The equilibrium model equation

for calculating the emission rate Equation (13) was used to calculate the emission rate, and then it was compared with the flux chamber measurement. The derivation of the equation for the equilibrium emission rate calculation is discussed in Section 4.

Wind Velocity and Solar Intensity Studies--

The second and third explanations were investigated with a series of precision and accuracy measurements during which the flux chamber parameters were held constant but the linear velocity of the SIS was changed. During the course of this study, the solar intensity was measured with a calibrated Kipp & Zonen Solarimeter located next to the SIS. Because controlling the solar intensity was beyond the resources and scope of this study, the levels were monitored throughout the study to see if any correlations could be found in emission rate, precision, or bias of the method. The air velocity in the SIS was controlled by a damper placed in the blower inlet duct, which was able to control an average air velocity in the SIS enclosure ranging from 0.22 to 0.56 m/s. A series of three different velocities was measured with two flux chambers, and the velocity measurements were repeated each day for three days. The percent bias, Equation (16), was calculated at each SIS velocity.

Liquid Surface Flow Study--

An experiment was conducted to determine if the flux chamber affected the liquid surface motion of the SIS and if this affected the emission rate from the surface. The surface motion or drift velocity was monitored and measured by using pieces of wax paper floating on the surface with and without the flux chambers. The effect this had on the emission rate was determined both theoretically from models of the phase transfer process and experimentally by making SIS measurements while the flux chambers were on the surface.

FIELD EXPERIMENTS

The flux chamber method was evaluated at two sites in the field to determine the precision of the method under field conditions. The two sites that were chosen for the evaluation varied greatly in their design, purpose, and environmental conditions. Site One was a wastewater treatment facility for a chemical manufacturer in the Southeast; its field evaluation was

performed during December. Site Two was a waste stabilization treatment facility in the Midwest accepting liquid and sludge waste from a variety of industries; its field evaluation was made during June.

Site One: Chemical Manufacturing Wastewater Treatment Facility

The flux chamber testing at Site One was made at a surface impoundment and a channel between an equalization basin and several activated sludge ponds. Figure 3 is a schematic of the wastewater treatment facility showing where the measurements were made. Two waste influents emptied warm wastewater from several batch operating processes into the surface impoundment. The wastewater always consisted of the same compounds, but the amount of organic material being added varied throughout the day. Occasionally, a separate organic layer would form on the liquid surface. Four flux chambers were placed at equal distances from the two waste influents by suspending the chambers from two support ropes. The surface being measured contained no visible organic layer. The chambers were placed in the points of a square with 1.5-m sides.

Two sets of flux chamber measurements were made at the same locations on the surface impoundment. The first was made at 2 p.m. on December 17, 1987, while the sun was directly hitting the chamber. The second measurement was made the same day at 4 p.m. after the sun had set behind a hill. The temperatures were 15 °C and 7 °C for the liquid and ambient air, respectively, during the first measurement, and 19 °C and 6 °C for the second measurement. On the second day of sampling at Site One, two sets of measurements were made from an open channel where wastewater overflowed from an equalization basin to a series of activated sludge ponds. The contents of the equalization basin were being mixed and aerated with heated air to prevent the waste from freezing. The four flux chambers were lowered onto the surface of the channel from a catwalk. The floats were removed because of the limited space in the channel, and no direct sunlight hit the liquid surface during the hours tested. The channel's emissions were initially measured at 12:30 p.m. on December 18 and later that day at 3:30 p.m. The temperature of the liquid was 27 °C at 12:30 p.m. and 26 °C at 3:30 p.m. The ambient air temperature was 7 °C at both 12:30 p.m. and 3:30 p.m.

Between measurements at the surface impoundment and the channel, two QC check samples were collected. A method blank was prepared by passing zero air

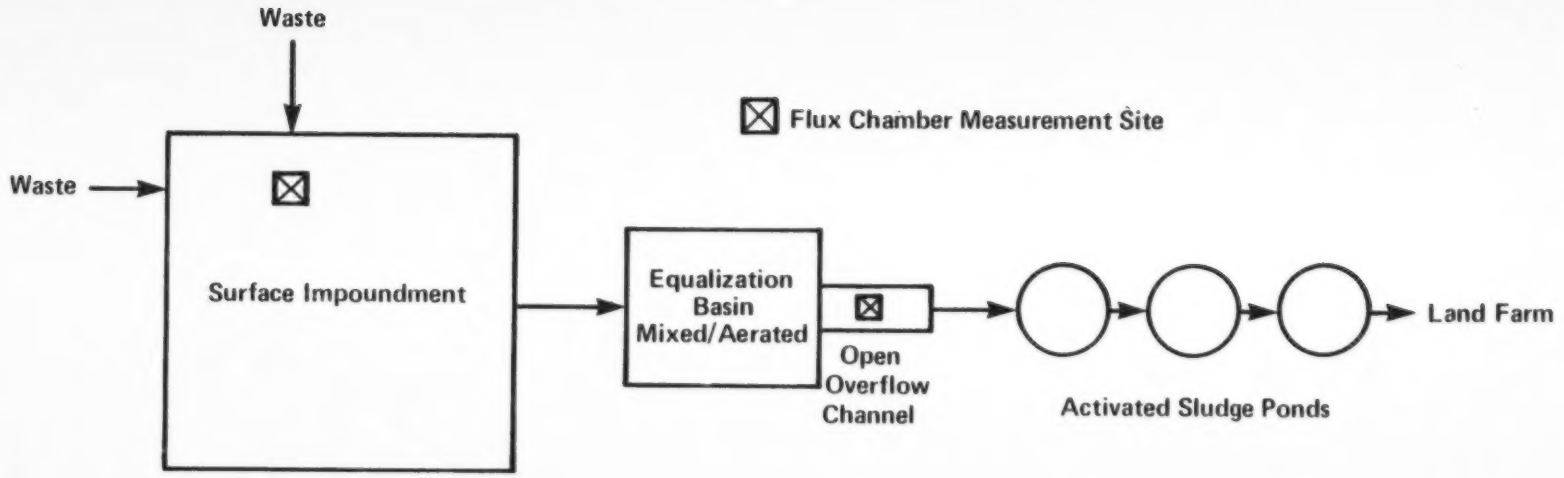

Figure 3. Schematic of Site One wastewater treatment facility.

through the sweep gas and sample lines and collecting it in a canister as if it were a flux chamber sample. A system QC check sample was prepared by passing a QC standard through the sample line and collecting a canister sample as if it were a flux chamber sample. The QC standard contained the major volatile compounds identified in the wastewater during the presite visit.

Site Two: Waste Stabilization and Treatment Facility

The second site used to evaluate the flux chamber method had open storage tanks containing a variety of liquid wastes. Figure 4 shows a schematic of the waste treatment process. Liquid waste from a wide range of sources was delivered and stored in two open tanks, one containing RCRA waste classified as hazardous and the other classified as nonhazardous. The liquid waste was mixed with lime and flue ash to form a manageable solid waste. The solid was temporarily stored on-site before disposal at an authorized landfill. Runoff from the stored solids was collected in open tanks and treated to remove organics. The treated runoff water was then stored in open tanks until it could be disposed of. Because of its higher level of volatile emissions, the nonhazardous storage tank was chosen for flux chamber measurements. One of the primary runoff tanks was also chosen to evaluate the method for a low- level source. All the tanks were 4.3 m high, had a diameter of 9 m, and could hold 280 m^3 (75,000 gal). The flux chambers were suspended from support ropes and floated on the liquid surface.

For the first day of testing, the flux chambers were evaluated on the runoff tank. Emission measurements were made at 2:30 p.m. and 4:20 p.m. on June 8, 1988. The tank was filled to a depth of approximately 1.5 m. Hazy sunlight was hitting the surface during the first measurement, and it was cloudy during the second measurement. The liquid surface temperature was a consistent 21 °C for both measurements; the ambient temperature was 20 °C for the first measurement and 17 °C for the second measurement.

The nonhazardous waste storage tank was measured the second day at 12:30 p.m. and 3:30 p.m. on June 9, 1988. The liquid surface was dark and oily, but there was a single continuous layer on the surface. Between the 12:30 p.m. measurement and the 3:30 p.m. measurement, a waste delivery was made to the tank, thus slightly raising the level. The approximate depth of the tank contents was 3 m. The sun was shining during both measurements and the ambient temperature was 17 °C for the first and 19 °C for the second measurement. The liquid surface temperature was 43 °C during the first

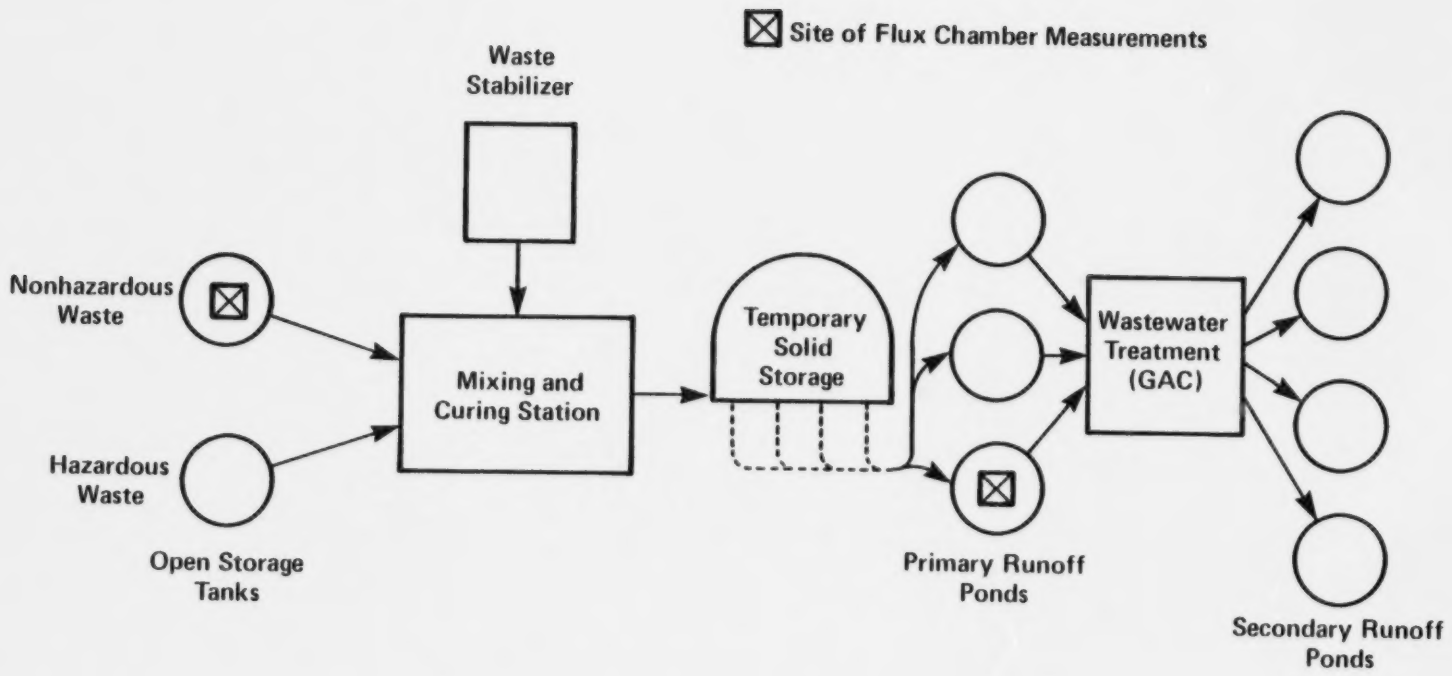

Figure 4. Schematic of Site Two waste stabilization and treatment facility.

measurement and 49 °C for the second. The same QC check and blank procedure was followed at Site Two as at Site One except that the QC standard was a certified mix of five organic compounds not necessarily representing those present in the waste because of the daily changing composition of the waste at this site.

For both field tests, the precision of the flux chamber method was calculated by determining variability of the measured emission rate between the collocated flux chambers. The variability due to sample collection and storage and instrumental analysis was also determined by collecting replicate samples and performing replicate analyses of the samples.

In determining the field precision of the flux chamber method, three levels of variability were analyzed. These levels included the time of day, the different flux chambers, and the replicate measurements within the flux chambers. The time of day variable had two levels: early and late. Within each time of day level were the 4 replicate flux chamber samples. This takes on a hierarchical structure that was analyzed by the NESTED procedure available with the Statistical Analysis System software package. The NESTED procedure was specifically designed to perform an analysis of variance and an analysis of covariance for data from an experiment with a nested (hierarchical) structure.

The output from the NESTED procedure reported the variance components associated with the different levels of variability described above plus the instrumental analysis variability. These variance components, along with the concentration mean for the compound in question, have been used to compute a coefficient of variation for both the total variability and the sample measurement error that were determined for each compound. The total variability between flux chamber measurements was computed by summing the variance components that measured the variability between chambers with the variance components that measured the variability in the sample measurement process. The sample measurement variability corresponds to the variability between the laboratory measurements of the replicate samples that were taken within a single flux chamber, and the instrumental analysis variability was determined from replicate analyses of a single sample.

SECTION 6

RESULTS AND DISCUSSION

LABORATORY RESULTS

The laboratory evaluations were conducted to determine if the flux chamber and SIS were functioning properly, to optimize the operating parameters, to estimate the method's precision and accuracy, and to investigate the reasons for the measured bias in the flux chamber results.

Flow Rate and Mixing Studies

The most critical factors when using the flux chamber and the SIS to measure emission rates are accurately knowing the flow rate through the enclosures and obtaining a well-mixed, representative sample from the enclosures. The sweep gas flow rate in the flux chamber was easily measured by directly using a mass flow meter or rotameter and was periodically checked by using a bubble flow meter. These flow rate methods are accurate to within 2 percent if the instruments are properly calibrated and the methods are performed correctly. Mixing within the flux chamber has been a matter of much study and concern. Several authors have recently concluded that the design used in this study provided excellent mixing (16, 20), and the results of this study confirm those findings. Visual observation using a smoke stick showed that the sweep gas converged in the center of the chamber and the resultant turbulent flow filled the chamber with smoke.

Two analytical approaches were taken to ensure that complete mixing was occurring in the flux chamber. First, a tracer was introduced in the chamber at several different rates, and the emission rates were calculated using the flux chamber method. The actual rates varied from 40.9 to 137 mg/min/m^2. Table 4 compares the measured emission rate with the actual rate. The low RSD of the measurements indicates a steady-state concentration had been reached. The percent difference between the measured

TABLE 4. PROPANE TRACER STUDY IN THE FLUX CHAMBER

Actual emission rate ($mg/min/m^2$)	Measured emission rate (RSD) ($mg/min/m^2$)	Percent difference
40.9	38.9 (2.4)	-4.9
68.2	56.1 (1.6)	-17.8
96.9	81.5 (2.2)	-15.9
137	108 (1.2)	-21.3

RSD is the relative standard deviation in percent of four replicate measurements.

and the predicted emission rates was 21 percent or less. The small difference found indicated complete mixing had been achieved.

The second approach was to collect the samples from different points inside the chamber and determine if a spatial concentration gradient existed. Table 5 compares the emission rates calculated for 1,1,1-trichloroethane from a flux chamber with the standard outlet configuration and from a flux chamber where the outlet position was varied. The only significant difference found was in the position closest to the surface, where the emission rate was measured to be 23.6 percent higher. This indicates that complete mixing has occurred at a level between 2 and 9.5 cm above the liquid surface, but within 2 cm of the emission source there may be a zone where the concentration is higher than in the well-mixed zone.

TABLE 5. FLUX CHAMBER OUTLET POSITION STUDY

Outlet position (cm above surface)	Control ($mg/min/m^3$)	Experimental ($mg/min/m^3$)	Percent difference
Standard	2.35	2.32	-1.3
1.9	2.08	2.57	23.6
9.5	2.59	2.56	-1.0
13.3	2.60	2.72	4.6
21.6	2.67	2.69	0.8

Measuring the flow rate through the SIS was not as direct as measuring it through the flux chamber; so, two separate approaches were used. A chemical tracer technique was used to calculate the flow rate in the SIS and an average velocity was measured with a standard Pitot tube.

The first method introduced a tracer gas, propane, into the SIS at a known flow rate and measured the concentration at the sampling port. If complete mixing and no loss of propane are assumed, the SIS flow rate (F_{sis}) can be determined from the concentration by using the following equation:

$$F_{sis} = F_{propane}/C \quad (17)$$

where $F_{propane}$ = flow rate of pure propane, mL/min
C = SIS concentration, mL/m^3

Three different flow rates of pure propane were introduced, and the results are shown in Table 6. For the propane flow rates introduced, the calculated SIS flow rate varied by an RSD of 5 percent. A linear regression of propane flow rate and measured propane concentrations resulted in a correlation coefficient of 0.99998, indicating complete mixing had occurred in the blower duct where samples are collected.

TABLE 6. PROPANE TRACER RESULTS FOR THE SIS

Propane flow rate (mL/min)	Measured concentration (mL/m^3)	Calculated SIS flow rate[a] (m^3/min)
168	7.87	21.4
326	16.3	20.1
552	28.6	19.3

[a]SIS flow rate was measured to be 22.1 m^3/min with a Pitot tube method.

The second flow rate measuring method used was the standard Pitot tube. The Pitot tubes were placed in the blower duct where the velocity was the greatest. The blower duct was traversed from the center to the wall to find the region where the velocity goes to zero. Four points between 0 and 3.2 cm from the wall were plotted versus velocity. The region from 2.2 cm to the center of the duct showed no measurable difference in velocity. At 0 cm the velocity was assumed to be zero and the first measurable reduction in velocity occurred at 3.2 cm. The area under the curve of velocity versus radius was integrated assuming straight lines between each point. This area was then divided by the velocity measured at the center of the duct to

obtain the effective radius. The effective radius was calculated to be 9.4 cm compared to the actual radius of 10.2 cm. A single center pitot reading was then used with the effective radius to calculate a flow rate. The effective radius acts as a correction factor to correct for the lower velocity at the duct walls. A flow rate of 22.1 m^3/min was calculated for the SIS blower during the propane tracer study. Comparing this calculated rate with the average value of the propane tracer study, a difference of only -8.2 percent was found. The agreement between the two different methods indicates an accurate flow rate measurement can be made using a single Pitot reading.

Parametric Studies

Before the accuracy and precision of the flux chamber were evaluated, several simple experiments were performed to determine which operating parameters affected the measured emission rate. All the parametric studies were performed with just 1,1,1-trichloroethane and water in the SIS except the flux chamber depth study. Several SIS parametric experiments were performed to determine if the SIS could be used to evaluate the accuracy and precision of the method. These included a sample outlet position study, a surface emission and concentration profile, and a vertical concentration profile. To ensure that an accurate total emission rate for the SIS could be calculated, a well-mixed sample had to be collected. Duplicate samples collected 1.9 cm from the near blower duct wall, the center of the duct (10 cm from the wall), and 1.9 cm from the bottom of the duct wall were analyzed. The percent difference between the average concentrations of the duplicate analysis was only 7.5 percent between sample outlet positions; however, the variance of the duplicates for the samples collected at the walls was much greater (50 percent) than the variance of the samples collected at the center (6.5 percent). Because of the increased precision, all other samples for this study were collected from the center of the duct.

To compare the results of flux chambers collocated on the surface of the SIS, it was important to determine if a spatial variation in the emission rate was occurring inside the SIS. The SIS was divided into three equal sections: an upwind, center, and a downwind section. A single flux chamber was used to measure the emissions from three different positions, each centered in one of the three section in the SIS. The total emissions from the SIS were measured concurrently with each flux chamber measurement.

The RSD of the three SIS measurements was 5.5 percent, and for the flux chamber measurements measured at three positions in the SIS the RSD was 3.5 percent. This confirms that there is no significant variation in the emission rates of the three sections and that the flux chambers collocated in these sections can be assumed to be measuring the same emissions. As an additional check, a liquid sample was collected from the surface of each of the three sections. The upwind and center samples had the same concentration, whereas the downwind sample concentration was 40 percent lower. This indicates that a depletion of 1,1,1-trichloroethane was occurring at the surface in the downwind sample, as theory predicts. This depletion should have an effect on the emission rate, but none was detected with the flux chambers, suggesting liquid surface flows may be altered from the semilaminar flow in the SIS with no flux chambers preventing the depletion from occurring. A concentration-depth profile in the center of the SIS was developed by determining the liquid concentrations at the surface, 19 cm deep and 37 cm deep. Concentrations determined at the surface and at 19 cm did not differ, and a 10 percent increase was measured from 19 cm to 37 cm, indicating that the liquid concentration exhibited a very slight (if any) concentration gradient from the organic layer on the bottom to the surface.

Flux Chamber Studies--

A detailed study of the flux chamber operating parameters has been previously reported (20); the present study was made to confirm those findings and verify that the new chambers were performing as designed. Sweep flow rate has been considered to be the most critical variable. Keinbusch and Ranum (20) found that flow rates between 5 and 10 L/min were the most accurate and that emission rates increased with flow rate. Dupont (16) recommends flow rates of less than 1 L/min to prevent pressure buildup.

The results of the flux chamber sweep flow rate study are shown in Table 7. Differential pressure readings were made at the sweep gas flow rate of 2, 5, and 9 L/min. The only measurable buildup was 2.0 Pa (0.008 in. of water) at the 9-L/min sweep flow rate. A large measured emission rate difference from the control was found for sweep flows lower than 2 L/min and fairly consistent results from 2 to 10 L/min. The difference from the SIS emission rate was consistent and negative, and the

TABLE 7. RESULTS OF SWEEP FLOW RATE STUDY

Flow rate (L/min)	Emission rate ($mg/min/m^2$)	Percent difference	
		From control[a]	From SIS
1.1	2.1	-48.0	-79
2.2	3.2	- 0.7	-69
2.2	2.8	-18.0	-73
3.4	0.76	- 2.2	-72
5.4	3.9	-14.0	-62
7.0	0.80	7.8	-71
9.3	0.73	-11.0	-73
10.4	3.9	4.5	-62

[a]Control was collocated flux chamber with a sweep flow of 5 L/min.

greatest difference was at a sweep flow rate of 1.1 L/min. These data agree with Keinbusch and Ranum's findings (20) and suggest an optimum operating range of sweep flow rate between 2 and 10 L/min. Pressure buildup at flows greater than 10 L/min with this flux chamber design prevents the use of higher flows. The large negative bias between flux chambers and SIS emission rates does not show a correlation with sweep flow rate, as was found in the study by Keinbusch and Ranum (20).

The time the flux chamber is on the surface with sweep gas flowing until the time a sample is collected can also influence the measured results. A time too short would result in incomplete mixing, and a time too long may result in depletion of the analyte at the liquid surface and excessive greenhouse heating of the liquid surface. Because emission rates were found to fluctuate with time, especially on a partly cloudy day, conditions were chosen to obtain a constant emission rate over the period of the study. Figure 5 is a graph of the measured emission rate versus time on a completely sunny day and a completely cloudy day. Little overall change in emission rate was seen with time. The variance between the highest and lowest values was 8 percent of the mean value for the cloudy day and 34 percent for the sunny day. A similar trend was found for both days. Initially, the rate was the lowest after 8 min and increased rapidly to a peak at 24 min on the cloudy day and 40 min on the sunny day. The rate gradually decreased from the peak. For the cloudy day, the initial increase may have been due to mixing of the emissions and the sweep gas, and the gradual decrease was probably due to depletion of the surface concentration

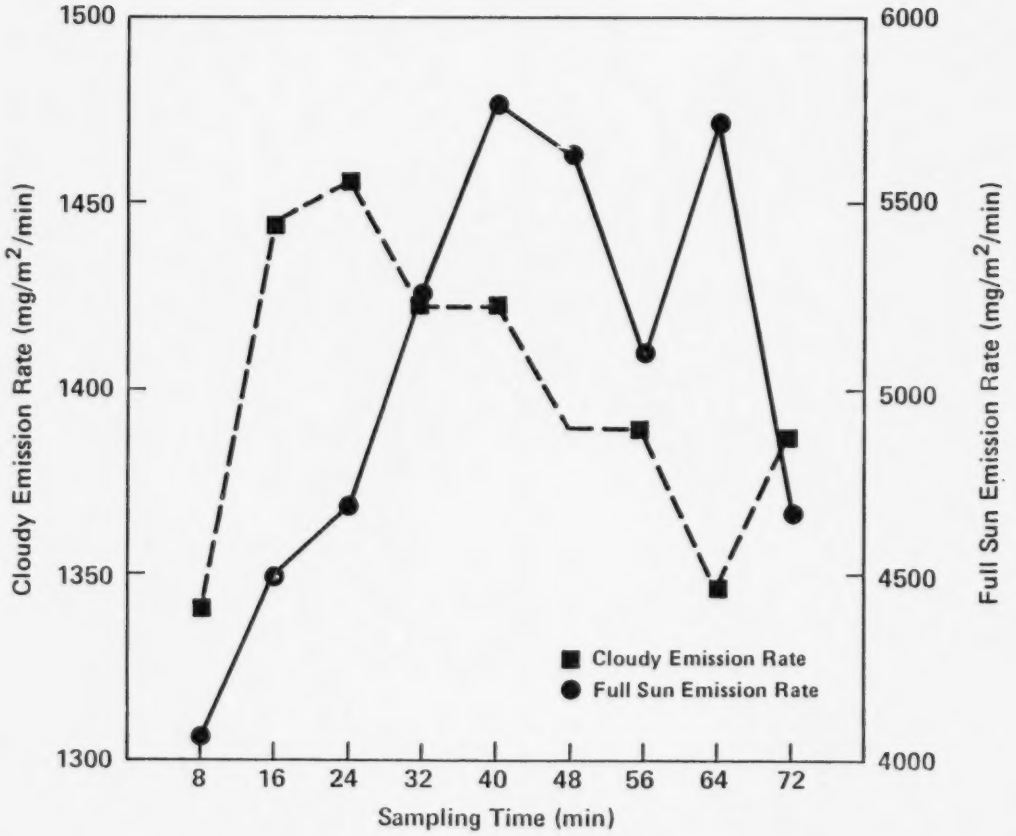

Figure 5. Measured emission rate versus sampling time.

of organic compounds. On the sunny day, the initial increase was also due to greenhouse heating of the liquid surface. The surface temperature of the liquid inside the flux chamber increased from 27 °C to a maximum of 31 °C at 32 min, and the air temperature inside the flux chamber rose from 29 °C to a maximum of 35 °C at 48 min during the sunny day. On the cloudy day, the inside liquid temperature remained constant, while the air temperature inside the flux chamber varied from 25 °C to 30 °C. The optimum sampling time would be when mixing is complete between 16 and 24 min and before greenhouse heating has peaked or surface depletion is detected at approximately 40 min. For all the laboratory studies and the field studies, samples were collected either at 20 min and 30 min and averaged or integrated between 20 and 30 min. The effect of sweep gas inlet height was found to be negligible. Table 8 shows the difference found between the control and the SIS at three different heights above the liquid surface. The largest variance (-7.5 percent) was found at the same height as the control, indicating that the small differences measured were insignificant. No trend was seen in the difference between the SIS measurement and inlet height. Because a lower inlet height should result in higher air velocities at the surface and no increase in emissions was found, the emission rate must be controlled by the liquid mass transfer coefficient. The air velocity in the flux chamber therefore must have little effect on the liquid-phase diffusion and turbulence at the liquid surface (low wind velocity conditions).

The depth of the flux chamber in the liquid was also found to have little effect on the measured emission rate. As previously noted, the three-component SIS mixture was used for this study; no trend was found in the measured emission rate with either the control or the SIS measurements for any of the three compounds. Table 9 shows the results for 1,1,1-trichloroethane. A consistent, negative bias was discovered by comparing the flux chamber with the SIS, and very good agreement was found between the two flux chambers. The fact that flux chamber depth has little effect on the measured emissions indicates that either the liquid-phase diffusion to the surface is occurring vertically and not horizontally inside the chamber or it is occurring at a depth of less than 1.3 cm. For all other studies and field evaluations, a depth of approximately 1.3 cm was used to minimize any isolation from the bulk solution, and yet ensure that the chamber remained in the water.

TABLE 8. SWEEP GAS INLET HEIGHT RESULTS

Height above liquid (cm)	Emission rate ($mg/m^2/min$)	Percent difference	
		From control[a]	From SIS
2.0	1.4	6.2	-58
6.4	1.5	-0.1	-56
10	1.5	-7.5	-57
10	1.3	-3.4	-63

[a]The control was 10 cm above the liquid surface.

TABLE 9. RESULTS OF FLUX CHAMBER DEPTH STUDY

Depth (cm)	1,1,1-Trichloroethane emission rate ($mg/m^2/min$)	Percent difference	
		From control[a]	From SIS
1.3	1.02	16.0	-72
2.5	1.07	1.4	-66
5.1	1.05	5.0	-62
8.9	1.02	3.5	-65

[a]Control was measured at a flux chamber depth of 1.3 cm.

Precision and Accuracy Studies

By using the optimum settings found during the parametric studies, a series of duplicate flux chamber measurements was made to estimate the method's precision and accuracy. Several factors were analyzed to determine if they had an effect on the method's precision and accuracy. Because a range of sweep flow rates was found to provide similar emission rates, the lowest (2 L/min), highest (10 L/min), and an intermediate (5 L/min) were investigated. Because the time study indicated that solar intensity may affect the method's performance, day and night measurements were compared. In addition to the single-component experiments mentioned above, a series of three-component measurements was also made.

A summary of the results of the precision and accuracy study is presented in Table 10. These data was grouped into similar samples and analyzed for precision and accuracy. Sample numbers 1-9 are grouped together because they have the same flow rate and a similar emission rate. Samples 10 to 12 have the same flow rate as samples 1 to 9, but they have a

TABLE 10. RESULTS OF FLUX CHAMBER PRECISION AND ACCURACY STUDY FOR 1,1,1-TRICHLOROETHANE

Sample #	Sweep flow rate (L/min)	Average emission rate ($mg/min/m^2$)	%CV	Bias (%)
1	5	14.3	2.1	-52
2	5	12.1	0.1	-45
3	5	13.2	1.5	-43
4	5	9.73	4.6	-25
5	5	9.75	6.0	-40
6	5	8.91	0.5	-56
7	5	7.47	4.8	-51
8	5	7.35	1.1	-40
9	5	7.63	4.8	-55
10	5	0.483	0.8	-76
11	5	0.506	6.3	-66
12	5	0.554	5.5	-60
13	2	1.14	3.9	-87
14	2	3.63	4.0	-78
15	2	6.74	4.3	-84
16	10	9.50	0.2	-46
17	10	9.57	1.9	-49
18	10	9.00	2.9	-54
19[a]	5	10.8	3.3	-47
20[a]	5	10.5	0.4	-56
21[a]	5	9.83	1.4	-68

%CV = percent coefficient of variation.
[a]Flux chamber measurements were made at night.

much lower emission rate. Samples 13 to 15 and 16 to 18 have sweep flow rates of 2 and 10 L/min, respectively. Samples 19 to 21 were collected at night at a sweep flow rate of 5 L/min. Table 11 contains the precision values estimated by using Equation (15) and the average bias for each group of data.

The method's precision was very good under all conditions tested. There was a slight increase in the RSD for the 2-L/min measurement and a decrease for both the 10-L/min and the nighttime measurements. The flux chamber accuracy was not as good as the precision. As seen previously, a consistent and negative bias was found. An increase in the bias was seen at 2 L/min and for the low emission measurements. The increase in the bias at 2 L/min is probably due to the concentration buildup inside the flux chamber which inhibited the emission rate. No improvement in the bias was found at the higher flow rate or at night, thus leaving no clue that would indicate a cause for a cause for the bias.

TABLE 11. PRECISION AND ACCURACY ESTIMATE FOR 1,1,1-TRICHLOROETHANE

Grouping	Number	Percent RSD[a]	Average bias (% + 90% CL)[b]
5 L/min, high emission	9	3.0	-45 ± 6.4
5 L/min, low emission	3	2.9	-67 ± 17
2 L/min	3	4.1	-82 ± 9.6
10 L/min	3	1.4	-49 ± 8.3
5 L/min, nighttime	3	1.5	-57 + 21

CL = confidence limit
[a] RSD is the pooled relative standard deviation.

To determine if multiple-component emissions affect the method's precision and accuracy, a three-component waste was generated in the SIS, and the precision and accuracy study was repeated. Table 12 shows the emission rates found and bias for each compound and each set of measurements. Table 13 gives the precision and accuracy estimates for the three-component study. The precision values were higher for the three-component study than for the single-component study. This difference could be due to the greater difficulty of analyzing three compounds with similar volatilities. The accuracy varied with compound, but a consistent negative bias was found. The bias for 1,1,1-trichloroethane was lower than in the single-component mixture. The emission rate for 1,1,1-trichloroethane in the three-component study was approximately 6 or 7 times the emission rate of the single-component study, suggesting that the bias may be dependent on emission rate. The polar MEK had the highest bias, and toluene's bias was -38 percent, which is substanitally different from the positive 30-percent average bias reported for toluene during a previous study (20). By adding the emission rates measured for all three compounds, a total organic emission rate was calculated. The precision of this value was good, and the average bias matched that found for 1,1,1-trichloroethane in the single-component study.

Negative Bias Investigation Studies

Several efforts were made to investigate the cause for the consistent, negative bias found for the flux chamber measurements. Several possible causes for this discrepancy were considered. Either the SIS or flux chamber emission measurements may not have been representative of the actual emission rate, or the flux chamber may have been suppressing the emission

TABLE 12. RESULTS OF THE THREE-COMPONENT PRECISION AND ACCURACY STUDY

	Methyl ethyl ketone			1,1,1-Trichloroethane			Toluene		
Sample #	Emission rate ($mg/min/m^3$)	CV (%)	Bias (%)	Emission rate ($mg/min/m^2$)	CV (%)	Bias (%)	Emission rate ($mg/min/m^2$)	CV (%)	Bias (%)
1	41.0	3.8	-62	94.0	10.0	-12	12.3	27.0	-33
2	32.7	6.1	-66	82.1	8.5	-11	10.2	13.0	-44
3	32.2	0.9	-63	60.2	11.0	-15	6.79	4.5	-47
4	23.6	20.0	-73	51.7	6.5	-41	6.17	7.6	-46
5	17.8	4.5	-74	48.4	9.7	-30	5.63	4.1	-41
6	14.7	1.5	-76	45.7	0.4	-25	5.19	3.0	-41
7	13.6	1.1	-65	48.6	5.3	-17	5.81	7.9	-27
8	12.0	3.6	-68	51.3	4.3	-16	6.32	3.7	-33
9	11.0	2.6	-66	53.1	7.9	-22	6.15	10.0	-32

CV = coefficient of variation.

TABLE 13. PRECISION AND ACCURACY ESTIMATES FOR THREE COMPONENT EMISSION MEASUREMENT

Compound	Number of replicates	Precision (%RSD[a])	Average bias (% + 90% CL)[b]
Methyl ethyl ketone	9	6.7	-68 + 3.1
1,1,1-Trichloroethane	9	11	-21 + 6.0
Toluene	9	13	-38 + 4.4
Total organic Content	9	8.6	-41 + 3.3

[a]RSD is the pooled relative standard deviation.
[b]CL is the confidence limit.

rate. The initial SIS flow, mixing, and emission profile studies reported earlier support the assumption that the SIS measurements were representative of the total emissions from the surface. The presence of the flux chamber on the surface could have inhibited the emission rate by three mechanisms.

First, the chamber could have inhibited the vapor-phase mass transfer as a results of both lower surface wind speeds inside the chamber and a concentration build-up inside the chamber. The flux chamber sweep flow rate study did reveal a concentration buildup effect at the lower flow rates, but no effect was seen with increasing the effective surface wind velocity during the inlet height study.

The second mechanism possibly responsible for the emission suppression could have been a suppression of the liquid-phase mass transfer. The depth of the flux chamber into the liquid could have affected the mass transfer, but no effect was seen during the depth study. The surface turbulence and flow patterns would also have affected the liquid-phase mass transfer, and positioning the flux chamber on the surface was likely to have altered both.

A third mechanism is that more solar energy could have been reaching the surface of the SIS without a flux chamber than one with a flux chamber because of the increased attenuation of the ultraviolet (UV) spectrum by the acrylic dome relative to the FEP film. The nighttime experiments, however, did not show any increase in accuracy.

Equilibrium Concentration Experiments--

The equilibrium concentration inside a flux chamber with no sweep flow was measured. Table 14 shows the average concentration calculated for two

TABLE 14. RESULTS OF EQUILIBRIUM CONCENTRATION DETERMINATION[a]

A. Average Concentrations (%CV)

Date	Phase	MEK (mg/L)	111-TCE (mg/L)	Toluene (mg/L)
1/16/87	Gas	0.106 (8.5)	4.10 (50)	0.522 (48)
	Liquid	64.8 (6.0)	463 (16)	56.6 (19)
3/26/87	Gas	0.321 (2.8)	2.26 (2.0)	0.388 (4.1)
	Liquid	130 (0.8)	46.9 (3.0)	8.48 (0.2)
5/1/87	Gas	0.857 (7.0)	0.893 (4.0)	0.145 (4.1)
	Liquid	984 (6.4)	142 (6.9)	26.0 (4.5)

B. Henry's law constants (atm m^3/mole)

Date	MEK	111-TCE	Toluene
1/16/87	3.97×10^{-5}	2.15×10^{-4}	2.24×10^{-4}
3/28/87	6.04×10^{-5}	1.18×10^{-3}	1.12×10^{-3}
5/1/87	2.11×10^{-5}	1.52×10^{-4}	1.35×10^{-4}
Literature values[b]	2.6×10^{-4}	4.92×10^{-3}	6.64×10^{-3}

[a]Abbreviation used:
CV = coefficient of variation
MEK = methyl ethyl ketone.
111-TCE = is 1,1,1-trichloroethane.
[b]Values taken from Reference (7).

flux chambers on three separate days. The gas-liquid phase equilibrium coefficient commonly known as the Henry's law constant (H), was calculated from the measured concentrations. The results reveal a large variation in the calculated H by this method, and most of the values are an order of magnitude less than literature values. This variation may be due to either a failure to reach equilibrium inside the chamber or an influence on equilibrium caused by parameters in the SIS or flux chambers. A constant concentration had been reached for each chamber, and residence times of approximately an hour were allowed before the equilibrium measurements were made. However, the constant concentration may have been due to a steady-state kinetic process and not a true equilibrium. Because the system was not closed, it would be difficult to ensure that a true equilibrium had been reached and that the concentrations measured were those at the point and time that equilibrium existed.

On the other hand, it is possible that equilibrium conditions existed and that the different values are due to real changes in the coefficient.

The literature values for H were obtained for a dilute single-component mixture in pure water under controlled temperature conditions. During the flux chamber measurements, a multicomponent mixture existed with widely varying concentrations of each component. Temperatures remained constant during the measurement, but they varied between measurements, and a difference in liquid and air temperature existed.

By using equilibrium Equation (14) and the equilibrium concentration, the emission rate was calculated. Two different approaches were taken to arrive at the emission rate. In addition to the concentrations at zero sweep flow, concentrations were measured at three other sweep flows between 0 and 9 L/min. One chamber remained at a sweep flow of 0, while the other was varied. Table 15 shows the emission rates calculated by the two different equilibrium approaches, the standard method, and the percent bias from the SIS measurements. Both equilibrium methods provided a more accurate value compared with the standard method. By Method 1 (Table 15) the C_o value measured in the flux chamber with zero sweep flow was substituted into Equation (13); the value of C_g at the highest sweep flow was measured, and E was calculated. The emission values calculated by the equilibrium methods showed a slight improvement in all cases, and a large improvement was seen in the value for MEK. By Method 2 (Table 15) the emission rate was calculated from the slope of the line when $1/C_g$ is plotted versus the sweep flow rate. Because some uncertainty exists in the measurement of C_o, no value for C_g at f=0 was plotted for the data shown in Table 15. Correlation coefficients of a linear regression of the lines were all greater than 0.96 except for MEK on May 1, 1987. The reciprocal of the intercept, which is equal to C_o, was found to be approximately 40 to 50 percent lower than the measured C_o.

These results indicate that a small amount of the bias is due to recondensation of the emitted compound in the flux chamber even at sweep flow rates as high as 9 L/min. The compound with the lowest variability, MEK, showed the greatest effect. To eliminate this problem, higher flow rates may be necessary, which have the disadvantages of raising both the internal chamber pressure and the detection limit of the method. Because no difference was found in the bias when the sweep flow was varied between 2 to 10 L/min, it is expected that a large increase would be necessary to realize a significant improvement.

TABLE 15. EMISSION RATE CALCULATION USING EQUILIBRIUM EQUATION ($mg/min/m^2$)[a]

Date	Compound	Method 1[b]	% Bias	Method 2[c]	% Bias	Standard method	% Bias
3/26/87	MEK	9.45	-37	9.35	-38	6.16	-59
	111-TCE	4.17	-53	4.46	-50	3.93	-56
	Toluene	1.08	-63	1.21	-58	9.81	-66
5/1/87	MEK	4.31	-37	72.7	7.1	23.8	-65
	111-TCE	6.30	-42	6.65	-39	5.45	-50
	Toluene	1.04	-78	1.11	-77	0.906	-81

[a]Abbreviations used:
MEK = methyl ethyl ketone.
111-TCE = 1,1,1-trichloroethane.
[b]Method 1 uses C_o and C at 10 L/min to calculate the emission rate.
[c]Method 2 plots 1/C versus the sweep flow rate and calculates the emission rate from the slope.

Wind Velocity and Solar Intensity Studies--

The accuracy of the flux chamber method was determined at three different SIS wind velocities and at different solar intensities. The results are shown in Table 16. No significant change in the bias was found due to wind velocity or solar intensity. Although there appeared to be a consistent increase in emission rate with increasing wind velocity, the bias of the flux chamber method does not appear to be affected. From the limited solar intensity data collected, no trend in accuracy or emission rate could be found. Correlation coefficients of 0.13, -0.36, and 0.032 for MEK, 1,1,1-trichloroethane, and toluene, respectively, were found between solar intensity and percent bias, indicating no correlation exists. The precision, like the bias, for the wind study was not affected by the velocity or solar intensity and matched that found during the precision studies. During the wind velocity study, an additional SIS measurement was collected while the flux chambers were sampling inside the SIS. Throughout the laboratory evaluation, SIS samples were collected before and after the flux chamber measurements, and an average of the SIS measurements was used to represent the true emission rate to determine the percent bias for the flux chamber method.

TABLE 16. RESULTS OF WIND VELOCITY AND SOLAR INTENSITY STUDY[a]

Wind velocity (m/s)	Solar intensity (W/m^2)	Emission rate (% Bias) MEK ($mg/min/m^2$)		111-TCE ($mg/min/m^2$)		Toluene ($mg/min/m^2$)	
0.21	9.5	1.13	(-71)	2.19	(-60)	0.50	(-58)
0.21	NA	3.77	(-87)	1.90	(-71)	0.62	(-65)
0.23	8.2	2.77	(-77)	3.41	(-49)	0.78	(-50)
0.39	4.6	1.41	(-72)	2.99	(-47)	0.66	(-57)
0.40	NA	6.43	(-82)	2.57	(-67)	0.72	(-69)
0.42	5.6	2.56	(-82)	2.35	(-62)	0.77	(-56)
0.51	NA	3.09	(-91)	2.93	(-60)	0.54	(-69)
0.52	NA	7.86	(-79)	3.16	(-78)	0.93	(-57)
0.54	8.0	2.96	(-83)	3.82	(-53)	0.88	(-48)
0.55	8.5	1.25	(-75)	2.28	(-64)	1.37	(-62)

[a]Abbreviations used:
NA = data were not available.
MEK = methyl ethyl ketone.
111-TCE = 1,1,1-trichloroethane.

Table 17 compares the SIS emission rate measured with the flux chambers present to the average of the before and after SIS emission rates. Seven of the nine measurements show a negative bias, and the average bias was -13.5 percent. This supports the assumption that the flux chamber suppresses the emission rate on the liquid surface, but the extent of the SIS bias is not close to that observed for the flux chambers. Because the two flux chambers cover only 14 percent of the SIS surface, it is logical to assume that only the covered portion is suppressed, and only a fraction of the flux chamber bias should be seen in the SIS measurement with the flux chambers. An emission rate (E') adjusted for the flux chamber emission rate (E_{fc}) can be calculated by using the following equation:

$$E' = E_{fc}\ (0.14) + E_{sis}\ (0.86) \qquad (18)$$

where E_{sis} = average of the SIS emission rate calculated before and after the flux chamber measurement.

TABLE 17. SIS EMISSION RATE MEASURED WITH FLUX CHAMBERS PRESENT

	SIS Emission Rate with Flux Chambers (% Difference from E_{sis})		
Wind velocity (m/s)	MEK ($mg/min/m^2$)	111-TCE ($mg/min/m^2$)	Toluene ($mg/min/m^2$)
0.21	26.0 (-7.9)	5.46 (-16)	1.87 (6.2)
0.40	32.2 (-11)	5.72 (-27)	1.81 (-21)
0.51	19.7 (-43)	9.22 (26)	1.26 (-28)

E_{sis} = average SIS emission rate measured before and after the flux chamber measurement.
MEK = methyl ethyl ketone.
111-TCE = 1,1,1-trichloroethane.

By comparing the emission rate values in Table 17 with the calculated E', an average bias of -3.8 percent is found. This suggests that the flux chamber is indeed suppressing the emission of the liquid surface being covered. The cause of the suppression, however, cannot be determined from this study.

Liquid Surface Flow Study--

The flow pattern of the liquid on the surface of the SIS was observed

without flux chambers present and with flux chambers. Without flux chambers a circular motion in a clockwise direction was observed with small eddies in the corners. The average time for a complete rotation was measured to be 4.5 min. When two flux chambers were placed in the SIS at their normal central positions, the clockwise circular pattern was noticed outside the flux chambers. Within a 15-cm radius behind the leeward flux chamber and between the two chambers, the surface was stagnant and small eddies prevented the liquid surface from this region to mix with the bulk liquid circulating around the chambers. The average time for a complete rotation of the outer surface was measured to be 6 min. The liquid surface inside the chamber was completely stagnant.

From these observations, it is clear that the flux chamber's presence in the SIS has an effect on the liquid surface motion. Emission theory indicates that surface turbulence can have a significant effect on the emission rate. Quantifying the extent of the emission perturbation due to the flux chamber is not possible because of the complexity of both the liquid motion and the emission processes. Extrapolating the flux chamber's effect on surface motion in the SIS to motion on a large open surface is not possible. Further studies are needed to determine if a similar effect is seen in the field.

FIELD EXPERIMENTS

Field studies were performed at two hazardous waste TSDFs. Each field study consisted of making four sets of four replicate flux chamber measurements under different environmental conditions. The first field study was performed at a site in the Southeast under the less than ideal conditions of cold temperatures and reactive compounds. Useful data and valuable experience were obtained during the initial field study. The second field study was conducted at a site in the Midwest under more favorable conditions, and better results were obtained. The field studies provided an accurate evaluation of the method's potential precision, as well as the practical precision due to the constraints of the field conditions and the complexity of the method.

Site One: Chemical Manufacturing Wastewater Treatment Facility

The presite visit to Site One indicated that the major compounds being

emitted from the source were reactive organic compounds containing oxygen and nitrogen. Lower levels of more stable compounds such as toluene and halogenated solvents were also found. Even though the reactive compounds may caused analytical problems, thus increasing the data variability, Site One was chosen for its convenient location and the availability of two emission sources containing the same organic compounds being emitted at very different levels (before and after heated aeration).

Because of several technical problems associated with simultaneously measuring emissions with four flux chambers on a surface impoundment, complete sample sets were not obtained. At the surface impoundment shown in Figure 3, the two sets of replicate data contained only three usable measurements per set because of a poor sample connection at one of the flux chambers. For one of the replicate sets at the overflow channel location, a flux chamber was not completely submerged into the waste, resulting in abnormally low emission rates for that chamber. As a result of these problems, a total of 13 flux chamber measurements were obtained instead of the 16 planned.

The compounds identified in the waste stream and chosen as target compounds were methylal (dimethoxymethane), chloroform, toluene, 2-heptanol, aniline, and nitrobenzene. Methylal, 2-heptanol, aniline, and nitrobenzene are relatively reactive compounds, and collection and analysis of these compounds with stainless steel canisters had not been evaluated. A QC check was performed to determine the recovery and stability of these compounds through the sample lines and in the canister. The results of this QC check are reported below. Some compounds were detected with an FID and some with an ECD. In the cases where compounds were detected with both detectors, the FID response was used except for chloroform, for which the FID response was very small.

The average emission rate measured and the percent RSD are shown for each measurement in Table 18. A small decrease in emission rate for each compound was found between the 2 p.m. and 4 p.m. measurements on December 17, 1987. This corresponds to a measured liquid temperature increase from 15 to 19 °C, an air temperature decrease from 7 to 6 °C, and a change from full sun to evening shade. In addition, waste was being added continuously, but no effort was made to monitor the influent concentrations. No significant change in the RSD was found between the two measurements.

TABLE 18. EMISSION RESULTS FROM SITE ONE FIELD EVALUATION

Compound	Surface impoundment (12/17/87)				Open Overflow Channel (12/18/87)			
	2 p.m.		4 p.m.		12:30 p.m.		3:30 p.m.	
	Emission Rate ($mg/min/m^2$)	(RSD)[a]	Emission Rate ($mg/min/m^2$)	(RSD)[a]	Emission Rate ($mg/min/m^2$)	(RSD)[a]	Emission Rate ($mg/min/m^2$)	(RSD)
Methylal	31.8	(3.0)	25.3	(6.4)	14.5	(2.7)	14.8	(3.0)
Chloroform	0.0471	(3.8)	0.0322	(5.4)	0.00219	(49)	0.00252	(7.3)
Toluene	0.0942	(4.9)	0.0533	(11)	0.00264	(14)	0.00247	(16)
2-Heptanol	0.136	(32)	0.101	(12)	0.0458	(0.3)	0.0426	(6.4)
Aniline	1.47	(37)	1.18	(20)	3.59	(34)	2.68	(26)
Nitrobenzene	0.113	(18)	0.100	(36)	0.132	(20)	0.115	(9.0)

[a]Only three measurements were averaged.

A large change in the emission rate was found between the surface impoundment and the open overflow channel for chloroform and toluene. A small decrease in emissions was observed for methylal and 2-heptanol, and increases or no changes were found for aniline and nitrobenzene. Chloroform and toluene are easily air-stripped from water during aeration because of their very low water solubilities and high vapor pressures. Aniline and nitrobenzene have relatively high water solubilities and low vapor pressures and would not be easily stripped during aeration. Both methylal, which has a very high vapor pressure and water solubility, and 2-heptanol, which has a low water solubility and a moderate vapor pressure, would be expected to have an intermediate capacity for being stripped during the aeration process. No significant change was observed in emission rate or RSD between the 12:30 p.m. and the 3:30 p.m. measurements on December 18, 1987. An increase in the RSD for toluene and chloroform was observed between December 17 and 18 measurements. This increase is probably due to the low concentrations being measured at the lower emission rates on December 18.

Precision Estimate--

The results from the Site One field evaluation were statistically analyzed as described in Section 5 to determine the variability and the sources of the method variability. Variation analysis was performed on the surface impoundment measurements as a group and on the open overflow channel measurements as a separate group. Table 19 lists the total coefficient of variation (CV) for each target compound in the surface impoundment and the CV due to the measurement technique used. The measurement CV is a combination of variance due to sample collection, storage, and instrumental analysis. The total CV includes measurement CV plus the variance between the chambers. Variability for methylal, chloroform, and toluene is less than 10 percent, with greater than 75 percent of the total variability being due to the measurement technique. 2-Heptanol, aniline, and nitrobenzene had CVs ranging from 43 to 51 percent, with greater than 90 percent of the variability due to the measurement technique. The results for the open overflow channel listed in Table 20 show greater variation for methylal, chloroform, toluene, and aniline and a larger percentage of variation due to the measurement. Inspection of the duplicate sample data, revealed that the duplicate canister's concentrations were significantly lower than the rest of the flux

TABLE 19. RESULTS OF VARIATION ANALYSIS FOR SURFACE IMPOUNDMENT EMISSION MEASUREMENTS AT SITE ONE

Compound	Coefficient of variation (Percent)	
	Total	Measurement
Methylal	6.04	4.71
Chloroform[a]	6.24	6.14
Toluene	9.26	7.95
2-Heptanol	50.8	50.8
Aniline	42.0	43.0
Nitrobenzene	45.9	42.4

[a]ECD results used in analysis.

TABLE 20. RESULTS OF VARIATION ANALYSIS FOR OPEN OVERFLOW CHANNNEL EMISSION MEASUREMENTS AT SITE ONE.

Compound	Coefficient of variation (Percent)		
	Total	Measurement	Total[a]
Methylal	30.1	30.1	3.57
Chloroform[b]	24.8	24.8	8.78
Toluene	19.4	8.21	18.3
2-Heptanol	30.3	30.3	5.63
Aniline	75.6	75.6	36.2
Nitrobenzene	39.1	39.1	18.4

[a]Duplicate canister sample data omitted.
[b]ECD results used in analysis.

chamber measurements. When those values are omitted, the total variability decreases; however, no estimate of the measurement variation is available because it is based on this duplicate sample analysis. The instrumental analysis variability was found to contribute less than 5 percent to the overall measurement variability, which means 95 percent or more of the measurement variability was due to sample collection and storage. The low concentrations measured could have been due to a leak in the duplicate sample collection manifold.

In conclusion, a relative precision of less than 10 percent was found for the total flux chamber method when measuring nonreactive VOCs. Over half of that variability is due to the sample measurement technique and not the flux chamber itself. Nitrobenzene, aniline, and 2-heptanol had greater variabilities due completely to the sample measurement technique used, which is confirmed by the QC results presented below.

Quality Control--

The QC procedures for Site One included a daily QC sample analysis, a single performance audit cylinder analysis, and blank analysis. The QC sample was prepared in the field by passing a standard through the sample lines and collecting it with the same procedure used for the flux measurements. The middle-level calibration standard was used to prepare the QC sample. Table 21 shows the percent recovery found for each compound on each day of analysis. Recoveries for the nonreactive compounds (chloroform and toluene) were excellent.

TABLE 21. RESULTS OF DAILY QC SAMPLE ANALYSIS

Compound	Theoretical standard concentration (mg/m^3)	Percent recovery		
		12/21	12/22	12/23
Methylal	1.40	194	203	188
Chloroform	0.316	104	104	99.4
Toluene	0.700	99.4	96.8	89.3
2-Heptanol	1.32	2.2	4.5	93.4
Aniline	1.35	142	145	53.3
Nitrobenzene	1.80	47.8	104	129

Methylal gave consistently high recoveries, which was probably due to sample carryover in the sample lines because the previous collected sample contained concentrations 100 times higher than the QC sample. 2-Heptanol, aniline, and nitrobenzene gave highly variable results, with recoveries varying from 2.2 to 145 percent. No trend was observed for these variations, and they probably result from a combination of poor stability in the calibration standard and the QC sample and of difficulties in analyzing the calibration standard and the QC sample. The concentrations in the actual samples were usually higher than in the QC sample, and the actual compound stabilities may be better than shown with the QC sample. Because of the high variability in the QC recovery, the emission rate measured with the flux chamber for 2-heptanol, aniline, and nitrobenzene may be of questionable accuracy and the precision estimate may be unusually large. An analysis of a QC performance audit cylinder containing chloroform and toluene reconfirmed that an accurate analysis for these compounds was being obtained. A sample blank was prepared by collecting sweep

gas through the sample lines bypassing the flux chamber. An analysis of the sample blank revealed small quantities of methylal and aniline. The concentrations of methylal was 4 orders of magnitude lower than the samples collected, and the aniline level was 0.5 percent of the level found in the samples. This low level of sample carryover did not affect the results of this study.

Site Two: Waste Stabilization and Treatment Facility

The presite visit to Site Two indicated that the site physically was suitable for testing and that volatile compounds were emitted from the liquid storage tanks. The major compounds present were not identified because the waste composition was likely to change. Because Site Two accepted waste for treatment from a variety of sources, no prediction could be made of what compounds would be emitted during the field test. For QC purposes and instrument calibration, a certified 18-component standard was used that contained a range of volatile hydrocarbons and halogenated organics. Two potential testing points were identified where high emission levels and low emission levels could be measured (Figure 4). Unfortunately, no correlation could be made between the composition of the high-level source (nonhazardous tank) and the low-level source (primary runoff tank).

After the samples were collected and analyzed, the major peaks not present in the 18-component standard were identified by gas chromatography/mass spectrometry (GC/MS) analysis. Quantification of the peaks not present in the 18-component standard was accomplished by determining the response factors relative to toluene, which was present in the 18-component standard, and then recalculating the peak concentrations. Two sets of the target compounds were chosen for this field study. For the primary runoff tank, acetone, 2-propanol, 1-butanol, toluene, o-xylene, methylene chloride, tetrachloroethylene, and total organics were the compounds chosen. For the nonhazardous tank, benzene, toluene, m,p-xylene, o-xylene, n-decane, limonene, n-undecane, 1,1,1-trichloroethane, and total organics were chosen. Because of the large number of compounds emitted from these two sources, a total organic value was calculated by summing all the FID peak area counts and using toluene's calibration factor.

During the first day of testing at the primary runoff tank, two sets of four replicate measurements were made with no problems. During the second

day's testing at the nonhazardous storage tank, one of the flux chambers in each of the two sets of replicates appeared not to have been completely submerged in the liquid. Liquid surface temperatures from that chamber matched those of ambient air and not the liquid surface, which was measured to be approximately 18 °C higher than the ambient air. The data are treated with and without this flux chamber included. The results of the primary runoff tank emission rate measurement are shown in Table 22. No significant difference in the emission rate or the RSD was found at the two different times. The major compounds being emitted were water-soluble oxygenated compounds. Most of the volatile compounds with low water solubility and high vapor pressure would have been lost to the atmosphere before reaching the primary runoff pond. The compound with the highest RSD had the lowest emission rate.

TABLE 22. EMISSION RATES MEASURED AT THE PRIMARY RUNOFF TANK AT SITE TWO

Compound	Average Emission Rate (RSD) 2:30 p.m. ($mg/min/m^2$)		4:20 p.m. ($mg/min/m^2$)	
Acetone	0.484	(10)	0.480	(12)
2-Propanol	0.641	(13)	0.686	(9.4)
1-Butanol	1.36	(12)	1.04	(15)
Toluene	0.0175	(9.4)	0.0174	(17)
o-Xylene	0.0031	(16)	0.00310	(17)
Methylene chloride[a]	0.0267	(14)	0.0263	(16)
Tetrachloroethylene	0.00085	(18)	0.00082	(19)
Total organics	3.32	(12)	3.22	(12)

[a]ECD was used to quantify this compound.

Table 23 shows the emission rates measured at the nonhazardous storage tank. Average emission rates and RSDs were calculated for each set of replicate measurements with and without the questionable flux chamber. No significant difference was found by comparing the emission rate and RSDs measured at 12:30 p.m. and 3:20 p.m.. An expected improvement in the RSD and an increased emission rate were found for the values calculated (omitting the questionable chamber). Emission rates in the nonhazardous storage tank were

TABLE 23. EMISSION RATES MEASURED AT THE NONHAZARDOUS STORAGE TANK AT SITE TWO

Compound	Average Emission Rate (RSD) 12:30 p.m. ($mg/min/m^2$)	12:30 p.m.[a] ($mg/min/m^2$)	3:20 p.m. ($mg/min/m^2$)	3:20 p.m.[a] ($mg/min/m^2$)
Benzene	0.128 (18)	0.141 (5.5)	0.137 (24)	0.155 (5.2)
Toluene	0.292 (18)	0.320 (7.9)	0.303 (21)	0.337 (8.9)
m,p-Xylene	2.09 (19)	2.28 (11)	2.25 (20)	2.50 (1.2)
o-Xylene	1.17 (19)	1.28 (11)	1.25 (21)	1.39 (7.6)
n-Decane	4.90 (22)	5.38 (14)	5.36 (20)	5.97 (5.3)
Limonene	6.10 (20)	6.62 (15)	6.63 (18)	7.31 (5.1)
n-Undecane	3.55 (26)	3.98 (16)	3.92 (22)	4.40 (5.2)
1,1,1-Trichloroethane[b]	0.131 (18)	0.144 (2.8)	0.114 (16)	0.123 (8.2)
Total organics	60.5 (22)	66.5 (14)	66.3 (21)	74.1 (5.4)

[a]Rates calculated omitting one chamber suspected to be invalid.
[b]ECD was used to quantify this compound.

much higher than those in the primary runoff tank. No major compounds being emitted were found to be oxygenated, water-soluble compounds. The oxygenated compounds, if present, would not become major emitters until the more volatile hydrocarbons were removed. By comparing the RSD from the primary runoff tank and the nonhazardous storage tank without the questionable chamber, slightly lower RSDs were found at the higher emission rates of the nonhazardous storage tank.

Precision Estimate--

The Site Two results were analyzed for variance as described in Section 5. The results from the primary runoff tank and the nonhazardous storage tank were treated separately, but the early and late measurements were treated together because little variation was found. The results for the primary runoff tank are listed in Table 24. The total CV for each target compound was found to vary from 13 to 19 percent, with approximately 60 percent of the variability being due to the measurement technique. The instrument analysis variability is listed; except for 1-propanol, 1-butanol, and o-xylene, the analytical variability contributes less than 5 percent, leaving sample collection and storage to account for 95 percent or more of the measurement variability.

TABLE 24. RESULTS OF VARIATION ANALYSIS FOR THE PRIMARY RUNOFF TANK EMISSION MEASUREMENTS AT SITE TWO

Compound	Coefficient of Variation (Percent)		
	Total	Measurement	Analysis
Acetone	13.1	6.72	0.32
1-Propanol	14.1	7.92	2.24
1-Butanol	14.7	7.03	0.74
Toluene	15.1	9.68	0.17
o-Xylene	18.0	14.5	5.87
Methylene chloride[a]	15.5	6.02	0.34
Tetrachloroethylene[a]	19.0	6.01	0.08
Total organics	14.7	7.3	0.05

[a]ECD results used in analysis.

Two separate variance analyses were performed on the nonhazardous storage tank emission results; one included the questionable flux chamber data and the other omitted it. Table 25 shows that when the questionable data are omitted, the CVs are similar to those found for the primary runoff tank; when the questionable data are included, the total variability increases by 5 to 10 percent. The measurement variability remains about the same and is higher than the primary runoff tank's measurement variability. This small increase in measurement variability is due to the problems of sampling and storage of the compounds with lower volatility, such as the xylenes, n-decane, limonene, and n-undecane. The instrumental analytical contribution to the measurement variance for the nonhazardous storage tank was less than 5 percent for all the target compounds.

Quality Control--

The QC checks for the field evaluation at Site Two included a field QC sample, field blank, and a sample stability check. Because the composition of the waste emissions was unknown, a QC standard was chosen at random; as it turned out, only one of the five components in the QC standard was found in the waste emission at each tank. Tetrachloroethylene was detected at low levels in the primary runoff tank, and benzene was detected in the nonhazardous storage tank. The QC standard was passed through the sample lines and collected in a canister just as a flux chamber sample would be

TABLE 25. RESULTS OF VARIATION ANALYSIS FOR THE NONHAZARDOUS STORAGE TANK EMISSION MEASUREMENTS AT SITE TWO

Compound	Coefficient of Variation (Percent)			
	Total	measurement	Total[a]	Measurement[a]
Benzene	22.4	10.4	9.74	9.74
Toluene	21.3	9.48	11.9	8.92
m,p-Xylene	21.2	8.51	13.8	8.04
o-Xylene	21.5	8.60	13.9	8.12
n-Decane	23.0	9.95	16.1	9.39
Limonene	21.4	10.3	16.4	9.75
n-Undecane	26.6	16.2	19.3	15.1
1,1,1-Trichloroethane[b]	NA[c]	NA	19.9	19.9
Total organics	23.7	14.9	16.9	14.0

[a]Omitted flux chamber data suspect of being invalid.
[b]ECD results used in analysis.
[c]NA = results were not available.

collected. Recovery for tetrachloroethylene was found to be 116 percent, and recovery for benzene was 99.2 percent, indicating that these compounds could be accurately collected and analyzed. Because a majority of the compounds could not be validated with the QC standard, a sample stability check was performed by analyzing a sample twice, once when it first arrived in the laboratory and again 5 to 7 days later. Table 26 shows the results found for samples from both tanks on analyses at two different days. These results show that all the compounds in both samples were stable over the period of analysis except for toluene, which showed a 50-percent increase in the primary runoff tank. This means the precision of the measurement should not be affected by the sample stability; however, the accuracy cannot be assessed from this study because the initial concentrations were not known.

Two blank samples were prepared and analyzed for the Site Two evaluation: a field blank and a trip blank. The field blank was prepared by passing zero air through the sample lines into a canister. Three of the target compounds were detected in the field blank. Limonene, n-decane, n-undecane, and total organics were all detected at concentrations less than 0.02 percent of the sample concentrations. The trip blank consisted of an evacuated canister sent to the field and brought back and analyzed without exposing it to the environment. Eight of the target compounds were detected in the trip blank. Toluene, m,p-xylene, o-xylene, n-decane, limonene, n-undecane, and total organics were found at concentrations of less than

TABLE 26. RESULTS OF SAMPLE STABILITY FOR SITE TWO

A. Primary Runoff Tank

Compound	Concentration (mg/m)^3		
	Day 5	Day 12	% Diff.[a]
Acetone	12.1	13.2	7.8
2-Propanol	17.8	19.7	9.9
1-Butanol	35.4	39.2	9.6
Toluene	0.444	0.939	52.7
Methylene chloride	0.755	0.696	-1.2
o-Xylene	0.095	0.094	-8.4
Tetrachloroethylene[b]	0.026	0.023	-12.8
Total organics	86.2	101	14.3

B. Nonhazardous Storage Tank

Compound	Concentration (mg/m)^3		
	Day 5	Day 10	% Diff.[a]
Benzene	3.21	2.84	-11.3
Toluene	7.08	6.30	-11.0
m,p-Xylene	47.7	43.5	-8.8
o-Xylene	26.7	24.4	-8.7
n-Decane	108.0	95.9	-11.2
Limonene	133	117	-10.9
n-Undecane	77.6	69.2	-10.9
1,1,1-Trichloroethane[b]	3.62	2.97	-18.1
Total organics	1320	118	-10.3

[a]% Diff = percent difference of day 10 from day 5
[b]This compound was quantified using the ECD.

0.1 percent of the sample concentration. 1,1,1-Trichloroethane was found at 1 percent of the sample concentration. These levels of contamination had no effect on the accuracy or precision of the method. The source of the contamination was determined to be due to carryover from the canister dilution system and was not a flux chamber problem.

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